

## REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-03-

Public reporting burden for this collection of information is estimated to average 1 hour per response, including gathering and maintaining the data needed, and completing and reviewing the collection of information, including suggestions for reducing this burden. To Washington Headquarters Services, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project 0704-0188.

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED	
	27-JUN-03	FINAL (01-JAN-2003 TO 31-DEC-2002)	
4. TITLE AND SUBTITLE		5. FUNDING NUMBERS	
OXIDE/OXIDE CERAMICS AND COMPOSITES MEETING		F49620-02-0088	
6. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NUMBER	
PROFESSOR A. SAYIR			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
CASE WESTERN UNIVERSITY 10900 EUCLID AVENUE CLEVELAND, OH 44108-7204			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		11. SUPPLEMENTARY NOTES	
AFOSR/NA 4015 WILSON BOULVARD ARLINGTON, VA 22203		BEST AVAILABLE COPY	
12a. DISTRIBUTION AVAILABILITY STATEMENT			
<p>Approved for public release; distribution unlimited.</p> <div style="text-align: right; border: 1px solid black; padding: 5px; margin-top: 10px;">20030731 091</div>			
13. ABSTRACT (Maximum 200 words)			
<p>Advanced materials are usually composite materials for structural components to carry loads and/or functional components to accomplish specific tasks. Oxide ceramic, oxide fiber reinforced ceramic composites and in-situ composites stand out as those which provide best properties in oxidizing environment. The oxide materials are essential to withstand severe loads in the oxidizing environment a severe conditions. The oxide ceramics and oxide composites is a crucial research area because it's importance to air breathing engine technology of US Air Force, Department of defense and US civilian industry. The components of the oxide ceramics and their composites are essential for the future aerospace industry and the information of their behavior is critical to understand the response of composites. Three focused topical session on the Oxide ceramics and Composites has been organized at the 27~ Annual Cocoa Beach Conference and Exposition on Advanced Ceramics &amp; Composites meeting. These sessions were:</p>			
<ul style="list-style-type: none"> <li>(i) Intrinsic Properties of Oxides (Magnetic, Electrical, Optical, Mechanical),</li> <li>(ii) Microstructures and Mechanical Behavior</li> <li>(iii) Novel Processing Techniques.</li> </ul>			
<p>The proposed meeting provided a forum for discussing the essential scientific issues involved in the development and use of high temperature materials.</p>			
14. SUBJECT TERMS		15. NUMBER OF PAGES	
16. PRICE CODE			
17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	

JUN 27 2003

# Final Report

**F49620-02-1-088**

## **Focused Topical Session: Oxide/Oxide ceramics and Composites Meeting**

**At the 27<sup>th</sup> Annual Cocoa Beach Conference and  
Exposition on Advanced Ceramics & Composites**

by

**A. Sayir**

**CASE WESTERN RESERVE UNIVERSITY**

**June 15, 2003**

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## Abstract

### **Focused Topical Session: Oxide/Oxide ceramics and Composites Meeting**

**At the 27<sup>th</sup> Annual Cocoa Beach Conference and Exposition on Advanced Ceramics & Composites**

**Cocoa Beach, FL**

**(1/26/2003 - 1/31/2003)**

Advanced materials are usually composite materials for structural components to carry loads and/or functional components to accomplish specific tasks. Oxide ceramic, oxide fiber reinforced ceramic composites and *in-situ* composites stand out as those which provide best properties in oxidizing environment. The oxide materials are essential to withstand severe loads in the oxidizing environment and severe conditions. The oxide ceramics and oxide composites is a crucial research area because it's importance to air breathing engine technology of US Air Force, Department of defense and US civilian industry. The components of the oxide ceramics and their composites are essential for the future aerospace industry and the information of their behavior is critical to understand the response of composites. Three focused topical session on the Oxide ceramics and Composites has been organized at the 27<sup>th</sup> Annual Cocoa Beach Conference and Exposition on Advanced Ceramics & Composites meeting. These sessions were:

- (i) **Intrinsic Properties of Oxides (Magnetic, Electrical, Optical, Mechanical),**
- (ii) **Microstructures and Mechanical Behavior**
- (iii) **Novel Processing Techniques.**

The proposed meeting provided a forum for discussing the essential scientific issues involved in the development and use of high temperature materials.

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## **Focused Topical Session: Oxide/Oxide ceramics and Composites Meeting**

High performance materials are usually composite materials. Oxide and oxide fiber reinforced composites stand out as those which provide the best properties in oxidizing environment. The fibers, matrices and the interfaces are the essential components in these materials and knowledge of their behavior is crucial to understand the response of composites as well as to develop new design strategies which optimize their use. The organization of three focused topical sessions on Oxide Ceramics and Composite at the 27<sup>th</sup> Annual Cocoa Beach Conference and Exposition on Advanced Ceramics & Composites (January 26/2003 through January 31/2003) was successful. The papers of the invited speakers are attached as an appendix and list of the presentation of these three sessions also included.

The purpose of this focused sessions was to bring scientists and engineers from all over the world together in order to gain an international perspective on new developments in the high temperature oxide ceramics field. There were two invited speakers from the United States, two from France, and one from Spain. The invited speakers are selected from esteemed university and research organizations on their respective continents. The list of invited speakers and the title of their papers are listed below:

1. Dickey, Elizabeth / Penn State University - USA  
"High-Temperature Residual Stress in Textured Oxide Composites".
2. Javier Llorca / Polytechnic University of Madrid - SPAIN

“Processing, Microstructure and Mechanical Behavior of Directionally-Solidified Eutectic Ceramic Oxides”.

3. Léo Mazerolles / CNRS - FRANCE

“Synthesis of Nanostructured Materials Based on Alumina”

4. *Marcelle Gaune-Escard / UISTI - FRANCE*

“Molten Salts: A Route to Tailored Ceramics”

5. Kenneth Sandhage, / OSU – USA

“Bioclastic Processing of Self-Assembled, Three-Dimensional Meso/Nanostructures with Tailored Chemistries”.

The main focus of the Oxide ceramics and composites was on the novel processing techniques. Good number of paper of papers on the mechanical characterization and microstructural analysis will be in session entitled Microstructures and Mechanical Behavior. The proposed meeting is expected to create a synergy between the scientist and engineers in the processing and microstructural characterization areas. An concerted effort has been dedicated during the planning time to invite the best processing scientists since their efforts usually have the long lasting impact on the community involved with the oxide ceramics and composites.

In addition to the invited speakers over 26 papers and associated abstracts from diverse backgrounds have participated at the focused topical session *Oxide/Oxide Ceramics and Composites*. In light of the imminent potential for oxide ceramic composites to advanced turbine engines and aircraft, three focused sessions were organized to bring scientists and engineers in the European community and Japan together with US researchers in order to gain an international

perspective on new developments in the high-temperature ceramics field. This provided a state-of-the-art picture of this rapidly evolving field of study. We coordinated this meeting with American ceramic Society and Air Force Office of Scientific Research to achieve productive results.

In addition, oxide material development is a paradigmatic topic in Materials Science, which needs for interdisciplinary research. In this respect, the focused oxide/oxide composite sessions was an attractive meeting point for chemists, physicists, and engineers.

## Oxide Ceramics and Composites

Session: **Intrinsic Properties of Oxides (Magnetic, Electrical, Optical, Mechanical)**  
**10:20:00 AM - 12:00:00 PM 1/29/2003**

*Lynnette Madsen*, "Opportunities in Ceramics".

*Elizabeth Dickey*, "High-Temperature Residual Stress in Textured Oxide Composites"  
Invited

*Robert Gall*, "Cu-Based Transparent Conducting Oxides of the Delafossite Structure".

*Robert Reeber*, "Corresponding States Principles for the Thermal Expansion of Oxides of MgO, CaO , SrO and BaO"

Session: **Microstructures and Mechanical Behavior**  
**1:20:00 PM - 6:00:00 PM 1/29/2003**

*Javier Llorca*, "Processing, Microstructure and Mechanical Behavior of Directionally-Solidified Eutectic Ceramic Oxides".  
Invited

*Kristin Keller*, "Evaluation of Dense Monazite Fiber-Coatings in Oxide-Oxide Minicomposites"

*Lee Pengyuan*, "The Rare-Earth Phosphate Coated Fiber for Oxide CMCs".

**Emmanuel Boakye**, "Monazite Coatings on Nextel 720 Fiber Tows: Effect of Precursor Morphology Coating".

**Richard Goettler**, "Properties of CMC with Scheelite and Uncoated Nextel 610 Fibers".

**Dong-Kyu Kim**, Fibrous Monoliths of Alumina -Mullite In Situ Composite Matrix-Aluminum Phosphate Interphase

**Pavel Mogilevsky**, "Anisotropy in Room Temperature Deformation and Fracture in CaWO<sub>4</sub> Scheelite".

**Javier Llorca**, "Deformation and Fracture Mechanisms of Single Crystal ZrO<sub>2</sub>(Er<sub>2</sub>O<sub>3</sub>)".

**Waltraud Kriven**, "In Situ High-Temperature Phase Transformation in YNbO<sub>4</sub>"

**Derek Northwood**, "The Effect of a High Strength Electric Field on the Low Temperature Degradation of a Y-TZP Ceramic".

**Hitomi Yamaguchi**, "Magnetic Field-Assisted Machining for Internal Parts of Alumina Ceramic Components".

**Paul-Francois Paradis**, "Contactless Density Measurement of Liquid Nd-Doped 50%CaO-50%Al<sub>2</sub>O<sub>3</sub>"

**Session:** Novel Processing Techniques  
8:00:00 AM - 12:00:00 PM 1/30/2003

**Jun Akedo**, "Aerosol Deposition (ADM) for Nanocomposite Material Synthesis: - A Novel Method of Ceramics Processing Without Firing".

**Léo Mazerolles**, "Synthesis of Nanostructured Materials Based on Alumina".  
Invited

**Maxim Lebedev**, "Al<sub>2</sub>O<sub>3</sub> - PZT Nanocomposite Mixture Ceramic Layer Fabricated Using Aerosol Deposition Method".

**Erik Bartscherer**, "Preparation of High Density Translucent PLZT Ceramics by Hot Isostatic Pressing".

**Cari August**, "Rheology of Fine Alumina Pastes".

**Marcelle Gaune-Escard**, "Molten Salts: A Route to Tailored Ceramics"  
**Invited**

**Rolf Janssen**, "Reaction Synthesis of Refractory Metal-Ceramic Composites".

**Kenneth Sandhage**, "Bioclastic Processing of Self-Assembled, Three-Dimensional Meso/Nanostructures with Tailored Chemistries".  
**Invited**

**Victor Orera**, "Ni and Co-ZrO<sub>2</sub> Composites Produced by Laser Zone Melting".

#### **POSTER SESSION**

**Magali Pinho**, "A Comparative Study of the Microstructure, Electric and Piezoelectric Properties of PZTCeramic Materials".

**Hathaikarn Choosuwan**, "Dielectric Relaxation and Thermal Expansion Properties of Niobium Based Oxides".

**Kazuya Tsujimichi**, "Mechanical and Electrical Properties of Al<sub>2</sub>O<sub>3</sub> Thin Films on Metals, Ceramics and Resins Prepared by Aerosol Deposition Method".

**Harry Gorter**, "Processing and Mechanical Characterization of In Situ Reinforced Alumina Composites".

**Antonio De Arellano Lopez**, "Room- and High-Temperature Tensile Fracture of Directionally-Solidified Chromia-doped Sapphire Fibers".

**Maria Gregori**, "Synthesis and Characterization of Z-Type Hexaferrite for Use as Microwave Absorber".

**Focused Topical Session: Oxide/Oxide ceramics and Composites Meeting  
Budget**

<b>Invited Speakers Addresses</b>	<b>Estimated Expenses: Travel, registration and lodging</b>	<b>Expected payment from AFOSR Grant</b>
Prof. Antonia Ramirez / Uni Seville SPAIN		\$600.00
Prof. Vcitor Orera / CSIC -SPAIN		\$600.00
<i>Marcelle Gaune-Escard / UISTI -</i> FRANCE		\$1,600.00
Prof. Léo Mazerolles / CNRS - FRANCE		\$1,000.00
Prof. E. Dickey / PSU USA		\$500.00
Prof. K. Sandhage / OSU USA		\$500.00
<b>Additional Speakers</b>		
Dr. A. Sayir / USA (Session Co- organizer) USA		\$2,577.00
Dr. Maria Souto / AUSTRIA		\$2,000.00
<b>TOTAL COSTED AMOUNT OF FUNDING</b>		<b>\$9,497.00</b>

# 27TH ANNUAL COCOA BEACH CONFERENCE AND EXPOSITION ON ADVANCED CERAMICS & COMPOSITES

*IN CONJUNCTION WITH THE  
ACERS ELECTRONICS  
DIVISION FALL MEETING*



Doubletree/Hilton Hotels  
Cocoa Beach, Fla.  
January 26-31, 2003

## Ceramics and Electronics for the New Horizon

From its humble beginnings more than a quarter century ago, the "Cocoa Beach Meeting" has grown in scope and stature to become the preeminent international technical meeting on advanced ceramics and composites. The "Cocoa Beach Meeting" is synonymous with leading edge research and development in these challenging technological areas. This year's meeting will continue the proud tradition of innovative R&D technical exchanges with three directed symposia and a series of focused topical sessions. In particular, to embrace the interdisciplinary needs between structural and electronic ceramics, this year's "Cocoa Beach Meeting" will be held in conjunction with the ACerS Electronics Division Fall Meeting, which will lead to exciting new and constructive cross-community interactions and research developments.

The Cocoa Beach Meeting is a completely open scientific forum for exchange of new ideas and findings. This year's meeting will highlight recent advances, developments, and field applications in engineering ceramics, composites, and electronics, and will emphasize a wide variety of ceramic materials and technologies for the new horizon. Authors are encouraged to submit presentation abstracts for consideration on any relevant topic. Anyone with an interest in ceramic-based materials, composites, or electronic materials is invited to participate including: scientists, engineers, technical and program managers, production and sales personnel, educators, and students.

Information regarding attendance arrangements will be available later this summer. Further information will be available on The American Ceramic Society's web site at [www.ceramics.org](http://www.ceramics.org).

## CALL FOR PAPERS

*Abstract Deadline: July 12, 2002  
Submit online at [www.ceramics.org](http://www.ceramics.org)*

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# Focused Topical Sessions

The following list of topics consists of technical sessions concentrated on specific areas of interest. The points of contact (POC) identified may be contacted prior to abstract submission to determine technical content relevance. Publication of the proceedings from the Focused Sessions will be included in the *Ceramic Engineering and Science Proceedings*.

## Product Development and Manufacturing of Advanced Ceramics and Composites

**Animesh Bose (POC), Materials Processing, Inc., USA**

Phone: 817/294-0135 • E-mail: [animeshbose@aol.com](mailto:animeshbose@aol.com)

**Elis Carlstrom, Swedish Ceramic Institute, Sweden**

**Charles Lewinsohn, Ceramatec Inc., USA**

Opportunities and issues on product development and manufacturing of advanced ceramics and composites will be emphasized:

- Approaches to technology analysis and manufacturing feasibility studies (including lifecycle analysis)
- Integrated component design and prototyping (design with ceramics, joining/assembly)
- Processing of advanced ceramics and composites (includes all near net shape processing and consolidation techniques)
- Novel applications for engineering ceramics and composites (unconventional components and compositions)

## Engineering Porous Materials

**Manuel E. Brito (POC), Synergy Materials Research Center, AIST, Japan**

Phone: 011-81-52-739-0135 • E-mail: [manuel-brito@aist.go.jp](mailto:manuel-brito@aist.go.jp)

**Heino Sieber, University of Erlangen-Nuernberg, Germany**

**Tatsuki Ohji, Synergy Materials Research Center, AIST, Japan**

The Engineering Porous Materials focused session will emphasize, but not be limited to, the following topics:

- Advances in processing of porous materials
- Structural characterization of porous materials
- Structure-mechanical and thermal properties relationships
- Applications and design issues for porous materials
- Industrial case studies

## Biomaterials

**Mineo Mizuno (POC), Japan Fine Ceramics Center, Japan**

Phone: 011-81-52-871-3500 • E-mail: [mizuno@jfcc.or.jp](mailto:mizuno@jfcc.or.jp)

**Gary Fischman, University of Illinois at Chicago, USA**

**Richard P. Rusin, 3M ESPE Dental Products, USA**

A coordinated forum for advances in biomaterials and technologies, technical and commercialization issues, and opportunities:

- Implants, coatings, cements and drug delivery
- Biomimetic materials and synthesis

**ABSTRACT DEADLINE: JULY 12, 2002**

- Dental ceramics
- Bioactive and bioinert ceramics
- Structure/properties of nature ceramic-based materials
- Behavior in biological environment (in vivo, vitro)
- Synthesis, processing, characterization and properties

## **Synthesis and Processing of Nanomaterials**

**William Mullins (POC), US Army Research Office, USA**

Phone: 919/549-4286 • E-mail: mullinsw@aro-emh1.army.mil

**Kazunori Kijima, Kyoto Institute of Technology, Japan**

**Rolf Clasen, University of Saarland, Germany**

A coordinated forum for advances in all aspects on the synthesis and processing of nanomaterials.

- Nanoscale synthesis
- Self-assembly, templated assembly and growth
- Nanopowders, nanostructured films and coatings
- Organic/ceramic structures
- Sintering of nanocrystalline systems
- Nanocomposite processing
- Modeling and simulation of system processing

## **Topics in Ceramic Armor**

**Jeffrey J. Swab (POC), US Army Research Laboratory, USA**

Phone: 410/306-0753 • E-mail: jswab@arl.army.mil

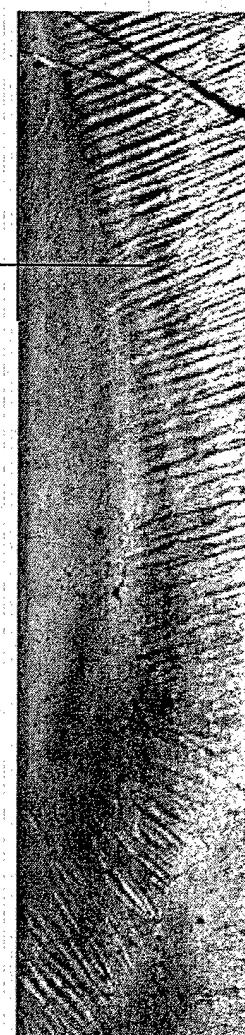
**James McCauley, Andrew Wereszczak, Jerry LaSalvia, Ernest Chin, US Army Research Laboratory, USA**

**Lisa Prokurat-Franks, US Tank and Automotive Research/Development and Engineering Center, USA**

**David Stepp, US Army Research Office, USA**

This annual topical session will bring together researchers from industry, academia, and government organizations working on opaque and transparent ceramic armor. Focused sessions will emphasize, but will not be limited to, the following areas:

- Processing and manufacturing
- Ultra-lightweight, high density and transparent ceramics
- Novel material concepts
- Penetration modeling
- Testing (impact, shock and high strain rate studies, etc.)
- Damage evolution and micromechanisms



## **Cocoa Beach Conference Program Chair**

**Dr. Hua-Tay Lin**  
Oak Ridge National Laboratory  
Metals and Ceramics Division  
Building 4515, Mail Stop 6068  
One Bethel Valley Road  
Oak Ridge, TN 37831-6068, USA  
Phone: 865/576-8857  
Fax: 865/574-8445  
E-mail: linh@ornl.gov

## **Electronics Division Program Chair**

**Dr. Dwight Viehland**  
Virginia Polytechnic Institute  
Department of Materials Science and Engineering  
201 Holden Hall  
Blacksburg, VA 2406, USA  
Phone: 540/231-2276  
Fax: 540/231-8919  
E-mail: viehland@mse.vt.edu

**CALL**

## Oxide Ceramics and Composites

Ali Sayir (POC), NASA Glenn Research Center, USA

Phone: 216/433-6254 • E-mail: ali.sayir@nasa.grc.gov

Joan Fuller, Air Force Office of Scientific Research, USA

Marie-Helene Berger, Centre Des Materiaux, Ecole des Mines de Paris, France

A coordinated forum to address various scientific and technical aspects related to multiphase oxide ceramics.

- Novel processing techniques
- Microstructures and mechanical behavior
- Intrinsic properties of oxides (magnetic, electrical, optical, mechanical)
- Polyphase oxide ceramics: processing and properties

## Fuel Cells: Materials, Developments and Applications

Co-sponsored by the Society for Automotive Engineering

Harlan Anderson (POC), University of Missouri-Rolla, USA

Phone: 573/341-4886 • E-mail: harlanua@umr.edu

Tim Armstrong, Oak Ridge National Laboratory, USA

Armin Reller, University of Augsburg, Germany

This session will focus on the recent advances in the scientific and technological developments, processing/properties, reliability, system design/applications, and field demonstrations and commercialization of the fuel cell materials. Specifically, contributions in the following topic areas are solicited:

- Materials processing and development of fuel cell materials
- Processing/microstructure/properties relationship
- Designing fuel cells for production/manufacturing
- Thermochemical reactivity and durability of fuel cells
- Modeling of materials transport and stability
- Environmental effects on long-term reliability
- Commercialization/demonstration status

## Gas, Chemical and Biological Ceramic Sensors

Girish Kale (POC), University of Leeds, United Kingdom

Phone: 0044-113-2332805 • E-mail: g.m.kale@leeds.ac.uk

Sheikh Akbar, Ohio State University, USA

Henk Verweij, Ohio State University, USA

This session will focus on ceramic materials and related technologies for sensors and use of these sensors in industrial applications and processes.

- Novel materials and designs for sensors
- Novel or improved fabrication techniques for sensors
- Novel types of sensors and/or new sensor applications
- Theory, modeling and simulation
- Sensor data analysis and packaging
- Intrinsic capabilities or limitations of sensors or sensor materials

**ABSTRACT DEADLINE: JULY 12, 2002**

# Symposium Topics

## Symposium I: Mechanical Behavior and Design of Engineering Ceramics and Composites

### Symposium Organizers:

Andrew Wereszczak (POC), US Army Research Laboratory, USA  
Phone: 410/306-0858 • E-mail: awereszczak@arl.army.mil

Mark Andrews, Caterpillar, USA

Ramakrishna Bhatt, US Army Research Laboratory, USA

Stephen Duffy, Cleveland State University, USA

Jurgen Heinrich, Technical University Clausthal, Germany

Michael Jenkins, University of Washington, USA

Akira Kohyama, Kyoto University, Japan

Walter Krenkel, DLR German Aerospace Center, Germany

Edgar Lara-Curcio, Oak Ridge National Laboratory, USA

### Sponsored by:

Engineering Ceramics Division, US Army Research Laboratory, DOE Office of Distributed Energy Resources

A coordinated forum for the presentation of advances in all aspects of the R&D of the performance evaluation of ceramics and composites and their application to structural component design. Specifically, contributions in the following topic areas are solicited:

#### • Performance Evaluation of Ceramics and Composites

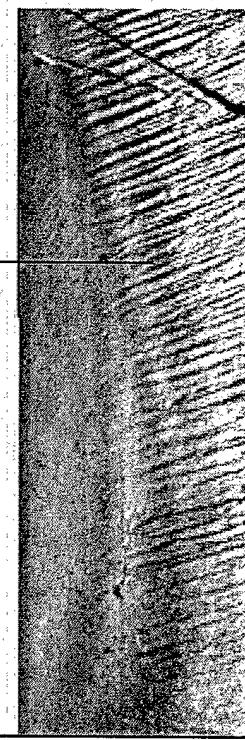
- Mechanical characterization
- Thermal response
- Damage evolution and its effects
- Residual and internal stresses and their effects
- Time-dependent properties and environmental effects
- Statistical variation in properties and performance
- Wear properties and interaction of ceramics with metallic components
- Advanced characterization methods (e.g., NDE methods to assess surface-subsurface strength limiting failure modes)

#### • Material and Property Modeling

- Microstructural and physics-based design
- Fiber architecture effects on predicted performance
- Interface mechanics
- Laminate and multiphase structures
- Control and engineering of residual stresses

#### • Design, Modeling and Testing of Structural Components

- Strength-size-scaling issues
- Flaw populations and data censoring
- Consideration of creep and fatigue



## Conference Papers

All conference papers will be published under one cover in the *Ceramic Engineering and Science Proceedings*.

All papers must be mailed to Society Headquarters by January 10, 2003.

Papers submitted at the meeting may not be included in the proceedings.

### Submit to:

Sarah Godby  
Cocoa Beach Manuscript  
The American Ceramic Society  
735 Ceramic Place  
Westerville, OH 43081-8720, USA

## Exhibit Opportunities

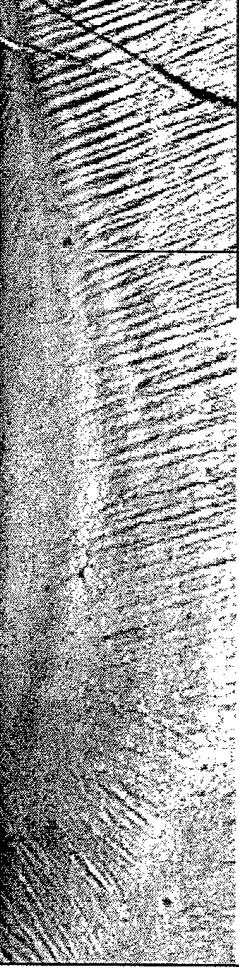
Reach 500 research and product development engineers involved in composites, advanced ceramics, electronic materials and structures. Two booth sizes are available in limited quantities: 8'x8' - \$800 and 10'x10' - \$1000.

The evening exhibits take place Monday and Tuesday, January 27 and 28, 2003, from 5:30-8 p.m. at the Hilton Hotel. A cash-bar and horsd'oeuvres reception takes place each night. On Monday, the conference poster session is held adjacent to the exhibit room. On Tuesday night, winners of the poster session are displayed in the Exhibit Hall.

For more information on Cocoa Beach marketing opportunities and to reserve your booth space, contact Peter Scott, sales manager, at 614/794-5844 or [pscott@acers.org](mailto:pscott@acers.org).

CALL

800-443-2763



- Proof testing, NDE analysis and quality assurance
- Case studies
  - IC and gas turbine engine applications
  - General structural applications
- When mechanical performance of a non-structural ceramic subcomponent can be a life limiter of the component's intended functionality (e.g., electronic devices, fuel cells, membranes, nuclear fission and fusion components, etc.)

Publication of the proceedings of this symposium will be included in the *Ceramic Engineering and Science Proceedings*.

## Symposium II: Advanced Ceramic Coatings for Structural, Environmental and Functional Applications

### Symposium Organizers:

Dongming Zhu (POC), NASA Glenn Research Center, USA  
Phone: 216/433-5422 • E-mail: [dongming.zhu@grc.nasa.gov](mailto:dongming.zhu@grc.nasa.gov)

Uwe Schulz, DLR-German Aerospace Center, Germany

Ellen Y. Sun, United Technologies Research Center, USA

Hartmut Schneider, DLR-German Aerospace Center, Germany

Jeffrey I. Eldridge, NASA Glenn Research Center, USA

Yutaka Kagawa, University of Tokyo, Japan

Kazuhisa Miyoshi, NASA Glenn Research Center, USA

Jitendra P. Singh, Argonne National Laboratory, USA

Narottam P. Bansal, NASA Glenn Research Center, USA

William J. Clegg, Cambridge University, UK

### Sponsored by:

Engineering Ceramics Division, NASA Glenn Research Center, DOE Office of Distributed Energy Resources.

This symposium will focus on recent advances in coating development, processing, microstructure and property characterization, and life prediction. Integrated structural, environmental properties and functionality through advanced coating processing and structural design are particularly emphasized. Specifically, contributions in the following topic areas are solicited:

- Thermal barrier coatings
- Environmental barrier coatings
- Nanostructured and smart coating systems
- Radiation barrier and thermal control coating systems
- Tribological coatings
- Advanced testing and non-destructive evaluation
- Interface phenomena, adhesion and failure mechanisms
- Micromechanics modeling and coating life prediction

Publication of the proceedings of this symposium will be included in the *Ceramic Engineering and Science Proceedings*.

### Hotel Information

A block of rooms has been reserved for meeting attendees at the following hotels. The group rates (per night) are available until January 4, 2003. Rates do not include the 10% sales tax.

#### DoubleTree Oceanfront Hotel

(Conference hotel)

Phone: 800/552-3224 or  
321/783-9222

Single/Double: \$99

Triple/Quad: \$115

#### Hilton Hotel

(Exhibition hotel; shuttle to DoubleTree provided)

Phone: 800/526-2609 or  
321/799-0003

Single/Double: \$105

#### Howard Johnson Express Inn

(Adjacent to DoubleTree)

Phone: 800/552-3224 or  
321/783-8855

Single/Double/Triple/Quad: \$75  
(Includes continental breakfast)

Be sure to mention The American Ceramic Society when making your reservations.

ABSTRACT DEADLINE: JULY 12, 2002

## Symposium III: Functional Ceramics

### Symposium Organizers:

**Clive A. Randall** (POC), Pennsylvania State University, USA  
Phone: 814/863-1328 • E-mail: car4@psu.edu

**Angus Kingon** (POC), North Carolina State University, USA  
Phone: 919/515-8636 • E-mail: angus\_kingon@ncsu.edu

Igor Kosacki, Oak Ridge National Laboratory, USA

### Sponsored by:

Electronics Division, Engineering Ceramics Division

The aim of this symposium is to critically review the state-of-the-art issues in functional ceramics. Specifically, proposed sessions will cover powder processing in electroceramics, dielectric materials and applications, piezoelectric transducers and actuators, conducting oxides, interfacial and scaling phenomena in electroceramics, and thin film ferroelectrics.

- Interfacial and scaling phenomena in electroceramics
- Microwave dielectrics and LTCC materials
- Conducting oxides: transparent oxides and ionic conductors
- Thin film ferroelectrics
- Piezoelectric transducers and actuators
- Modern challenges in processing electroceramics

Publication of the proceedings of this symposium will be included in the *Ceramic Engineering and Science Proceedings*.

## Abstract Instructions

Visit the ACerS web site at [www.ceramics.org](http://www.ceramics.org) to review the symposia descriptions and use the new Online Conference Management System. Follow these simple instructions:

- Click on Meetings & Expositions
- Click on Meetings Schedule and Information
- Click on Cocoa Beach: The 27th International Conference on Advanced Ceramics and Composites
- Click on Submit Abstracts
- Follow the system prompts to complete the online abstract form

Your abstract will be immediately available for review by potential attendees, co-participants and the program organizers. When your abstract has been accepted and scheduled, you will receive a confirmation e-mail.

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- At the top of an 8-1/2 x 11 inch sheet of white paper, type Cocoa Beach—The 27th International Conference on Advanced Ceramics and Composites.

- Double-space and type the **Session/Symposium Title** for which your abstract is submitted. This information is mandatory.
- Double space and type the **Title of Your Presentation**, using capital and lower case letters, indicating any special characters, subscripts or superscripts as appropriate.
- Double space and type the **Initials and Last Names, Affiliations and Countries of the Authors** in the order in which they are to appear when your abstract is viewed or published. Use an asterisk after the last name of the presenting author.
- Double space and type **Your Abstract**, single-spaced, with 1 inch left and right margins. There is no word limit to your abstract, however, do not exceed one page.
- On a separate sheet of paper, list **All Authors with Complete Mailing and E-mail Addresses**.
- E-mail, mail or fax both the abstract page and the author list to:

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## A Novel Bioclastic Route to Self-Assembled, 3-D Nanoparticle Structures with Tailored Chemistries: the BaSIC Process

Ken H. Sandhage

Professor, Dept. Materials Science & Engineering

The Ohio State University, Columbus, OH

**Abstract:** "Bioclastic" is defined as "of rock or similar material attaining its present form through the action of living organisms" (Websters 3<sup>rd</sup> New International Dictionary, unabridged). A novel, hybrid (biological + synthetic chemical) fabrication route is introduced that utilizes bioclastic preforms to generate chemically-tailored nanoparticle structures with complex, three-dimensional (3-D) shapes: the BaSIC (Bioclastic and Shape-preserving Inorganic Conversion) Process. This process is illustrated by converting diatom (biosilica) microshells into other compositions while retaining the starting microshell shapes and meso-to-nanoscale features.

Diatoms are single-celled planktonic algae that are ubiquitous to marine and freshwater environments (e.g., from arctic to equatorial conditions). Diatoms form intricate microshells (frustules) comprised of self-assembled nanospheres of amorphous silica. The number of extant diatom species is  $\approx 10^5$ , with each species forming a 3-D frustule possessing a unique shape and a distinct pattern of fine features (e.g., meso-to-nanoscale pores, ridges, channels, protuberances). Enormous numbers of identical frustules can be generated by the continued reproduction of a single diatom species (e.g., 80 replications =  $2^{80} = 1.2$  trillion trillion > Avogadro's number!). Such massively parallel and precise self-assembly of 3-D nanoparticle structures is highly attractive for nanotechnological applications. However, the range of potential applications is severely limited by the silica-based chemistry of diatom frustules.

The compositional limitation of diatom frustules is overcome in the BaSIC process by using fluid/solid conversion reactions to alter the chemistry, but not the shape or fine features, of the frustules. To demonstrate this process, capsule-shaped *Aulacoseira* diatom frustules have been converted into MgO, CaO, TiO<sub>2</sub>, ZrO<sub>2</sub>, and SiC with a retention of the capsule shape and features. Biosculpted silica structures with non-natural shapes, obtained by patterning with silaffins (peptides extracted from diatoms), have also been converted. Reactions leading to a variety of other ceramics have been identified. Such shape-preserving chemical conversion, coupled with genetic tailoring of diatom frustule shapes, would allow for the low-cost mass production of Genetically-Engineered Micro/nanodevices (GEMs) for numerous applications.

**Biosketch:** Ken H. Sandhage received a B.S. in Metallurgical Engineering with Highest Distinction from Purdue University and a Ph.D. in Ceramics from the Massachusetts Institute of Technology. Prior to joining OSU in 1991, Sandhage worked as a Senior Scientist on process R&D at Corning, Inc. and at American Superconductor Corporation. Sandhage's research at OSU has focused on novel reaction processing of a variety of ceramics and ceramic composites for biomedical, sensor, refractory, electromagnetic, and structural applications. He has received the Purdy (best paper) Award from the American Ceramic Society (1996), the Lumley Research Award from OSU (2002, 1997), and an Outstanding Materials Engineer Award from Purdue (1997). In 1999-2000, Sandhage was a Humboldt Fellow in the Advanced Ceramics Group at the Technical University of Hamburg-Harburg. He is a Fellow of the American Ceramic Society.

## Using ~~Microorganisms~~ to Manufacture 3-D Ceramic Microdevices

A novel, biologically-based approach for mass producing chemically-tailored, three-dimensional (3-D) ceramic microdevices with fine (meso-to-nanoscale) features is being examined in a collaborative research effort between the groups of Dr. Ken Sandhage (Ohio State University, Columbus, OH) and Dr. Morley Stone (Air Force Research Laboratory, Wright-Patterson Air Force Base, OH) through support provided by the Air Force Office of Scientific Research. This revolutionary process could open the door to low-cost microdevices for a host of DoD and commercial applications (e.g., optical, biomedical, sensor, microfluidic, catalytic).

The conventional production of microdevices has been focused on two-dimensional, layer-by-layer processes (e.g., micromachining by photolithography/chemical etching). Such processing is not well-suited for the fabrication of microdevices with complex, 3-D shapes. Nature, on the other hand, provides numerous examples of microorganisms that directly generate 3-D ceramic microstructures with complex shapes. The shapes of such "bioclastic" structures are a result of self-assembly that is directed by the microorganisms. Among the most dramatic examples of bioclastic structures are the microshells (frustules) of diatoms (*Bacillariophyta*). Diatoms are single-celled algae that populate a wide variety of aquatic environments (marine and freshwater; equatorial to arctic climates). Indeed, it is estimated that more than 20% of the carbon used to generate new primary organic matter on earth each year is tied up in diatoms. Each diatom cell contains a frustule comprised of a nanoporous assembly of amorphous silica nanoparticles (typically tens of nanometers in diameter). Each species of diatom assembles such nanoparticles into a frustule with a unique 3-D shape. Because the number of extant diatom species is estimated to be on the order of  $10^5$ , nature provides a tremendous variety of frustule shapes for potential microdevice applications (Figure 1). The maximum dimensions of diatom frustules can range from less than 1 micron (e.g., for *Chaetoceros galvestonensis*) to several millimeters (e.g., for *Ethmodiscus rex*). The frustules are decorated with fine, meso-to-nanoscale ( $<10^2$  nm) features, such as pores, ridges, channels, and protuberances, arranged in well-defined, species-specific patterns. Continued replication of a single parent diatom can yield enormous numbers of descendant diatoms, each of which would possess a frustule of the same shape. For example, 80 replications of a single parent diatom would yield  $2^{80}$  or  $1.2 \times 10^{24}$  (twice Avogadro's number!) similarly-shaped frustules. Such massively-parallel, precise, and direct fabrication of 3-D microstructures with fine (meso-to-nanoscale)

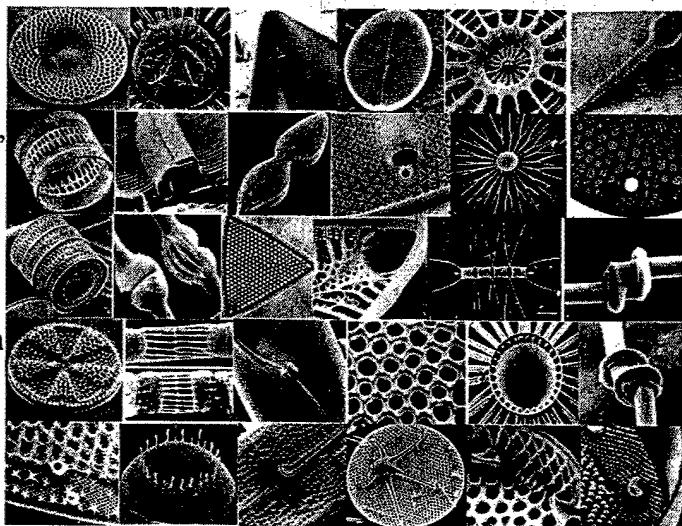


Figure 1. Secondary electron images of diatom frustules (reprinted with permission from F. E. Round, R. M. Crawford, D. G. Mann, The Diatoms: Biology and Morphology of the Genera, Cambridge University Press, 1990).

features under environmentally benign conditions is highly attractive for micro/nano-technological applications. However, the range of potential applications is severely limited by the silica-based composition of all diatom frustules.

The chemical limitation of diatom frustules has been overcome via a new process invented by Ken Sandhage, a professor in the Department of Materials Science and Engineering at Ohio State University, and his team of students. This new method, termed the BaSIC process (for Bioclastic and Shape-preserving Inorganic Conversion), utilizes certain chemical reactions to *convert diatom frustules into new compositions while retaining the original frustule shape and fine features*. One class of such reactions are oxidation-reduction displacement reactions of the following type:



where  $\{\text{Si}\}$  refers to silicon dissolved within a Mg-Si liquid (note: this Mg-Si liquid is a result of the continued reaction of the silicon, generated upon reduction of silica, with excess gaseous magnesium). This displacement reaction has been used to convert capsule-shaped frustules of the diatom *Aulacoseira* into magnesium oxide, as shown in Figure 2. The images in Figures 2a and 2b reveal that the overall shapes and fine features (nodules, protuberances, pores) of the frustules were well preserved after conversion into magnesium oxide. Image analyses of the fine pores running in rows along the *Aulacoseira* wall (Figs. 2a and b) revealed little change in the pore size distribution upon conversion. Indeed, the average pore size before and after conversion agreed to within 30 nm! Solidified Mg-Si liquid (the  $\{\text{Si}\}$  product of reaction (1)) can also be seen under a reacted frustule in Figure 2b. Because this liquid preferred to wet the metallic substrate more than the MgO, the liquid sweated away during reaction at 750-900°C, so as to yield monolithic MgO frustules. A higher magnification secondary electron image, revealing the crystalline nature and fine grain size (a few hundred nm) of the converted frustule, is shown in Figure 2c. An energy-dispersive x-ray (EDX) spectrum, revealing the presence of Mg and O in the converted frustule, is shown in Figure 2d (note: the small gold peak in this EDX pattern is due to a gold coating applied to the frustule to avoid charging). Transmission electron microscopy of ion-milled cross-sections confirmed the fine-grained nature of the MgO frustule, and the absence of residual silica or Mg-Si liquid within the converted frustule wall, after 1 hour of reaction at 900°C.

Work over the past year has demonstrated that the BaSIC process can be used to convert diatom silica into a variety of other ceramic compositions, including  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{CaO}$ , and  $\text{SiC}$ , while preserving the starting frustule shape and features. Examples of *Aulacoseira* frustules converted into zirconia and silicon carbide are shown below in Figures 3a and b, respectively. Thermodynamically-favored reactions leading to a number of other ceramics have also been identified and are under active study.

The BaSIC process has also been applied to biosilica structures with tailored (non-natural) shapes generated by Dr. Rajesh Naik and Dr. Morley Stone (Biotechnology Group, Air Force Research Laboratory, Wright-Patterson Air Force Base). A 19 amino acid peptide segment of a silaffin polypeptide, derived from the diatom *Cylindrotheca fusiformis*, has been found to dramatically enhance the rate of precipitation of silica from silicic acid solutions. By applying external forces (e.g., from flow fields, electric fields) during such precipitation, Naik and Stone

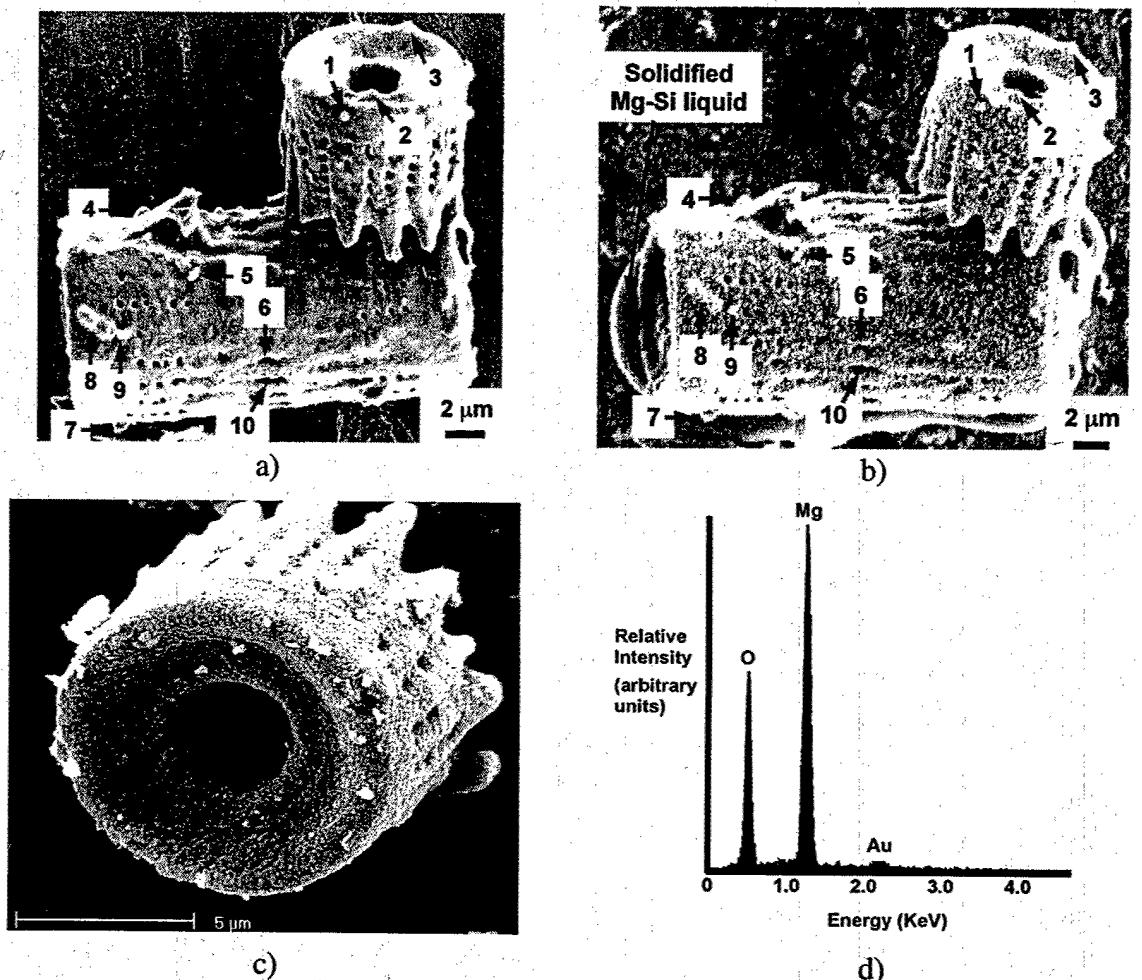


Figure 2. Secondary electron images of the same *Aulacoseira* diatom frustules: a) before and b) after conversion into  $\text{MgO}$  via reaction (1) at  $900^\circ\text{C}$ . Ten specific features are identified in the starting and converted frustules. A higher magnification image of a converted  $\text{MgO}$  frustule is shown in c). An EDX pattern obtained from the converted frustule is shown in d).

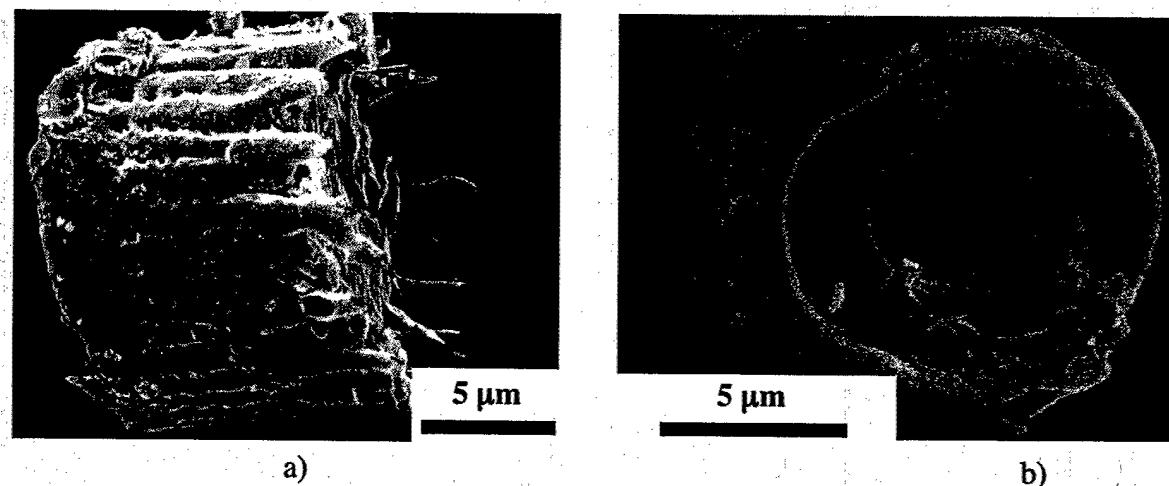


Figure 3. Secondary electron images of capsule-shaped *Aulacoseira* diatom frustules converted into: a)  $\text{ZrO}_2$  (side view of converted frustule) and b)  $\text{SiC}$  (end view of converted frustule).

have succeeded in sculpting the resulting biosilica into tailored shapes. For example, a multifilamentary biosilica structure, generated by forcing a solution of the peptide segment and silicic acid to flow in a pattern involving laminar shear, is shown in Figure 4a. This biosilica structure was then exposed to Mg(g) at 900°C. The resulting multifilamentary MgO is shown in Figure 4b. The general shape and multifilamentary nature were retained upon conversion into

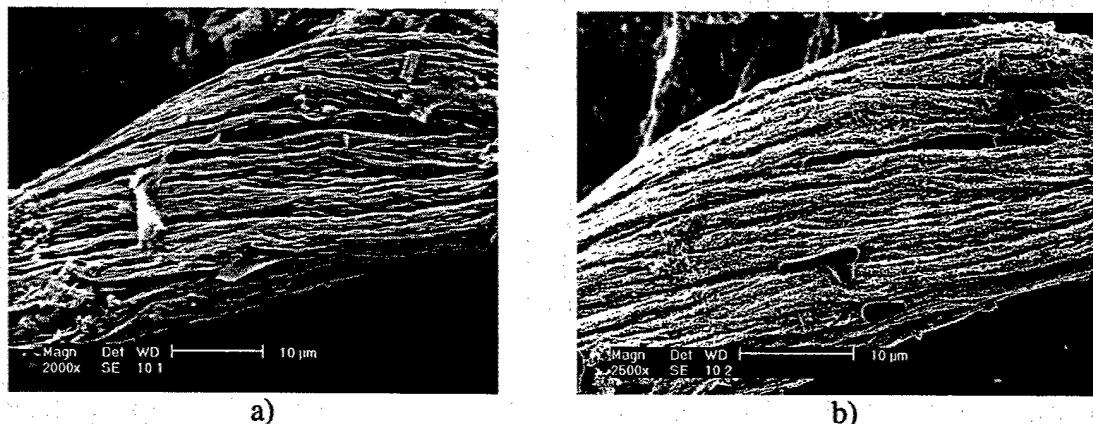


Figure 4. Secondary electron images of a biocatalyzed, multifilamentary silica structure: a) before, and b) after reaction with Mg(g) for 4 h at 900°C.

MgO. These images demonstrate that biosilica structures with tailored (non-natural) shapes may also be converted into other ceramics with a retention of the starting shapes and fine features. That is, peptides derived from diatoms may be used to “biosculpt” silica structures with tailored shapes that, in turn, may be converted into desired compositions through shape-preserving reactions. *This novel biosculpting and reactive conversion approach opens the door to a wider variety of ceramic shapes and compositions than are available in nature*, so that a broader range of potential microdevices may be produced that are of interest to the U.S. Air Force (e.g., sensors, biodegradable microcapsules, etc.).

The BaSIC process merges the attractive characteristics of biology (i.e., rapid, directed self assembly of precise 3-D nanoparticle structures under ambient conditions) with those of synthetic reaction processing (i.e., low-temperature, near net-shape conversion of ceramic preforms into new compositions) to yield complex-shaped 3-D nanoparticle structures with tailored chemistries. A schematic illustration of a BaSIC manufacturing process is shown in Figure 5. Microorganisms, like diatoms, may be used as biofactories to generate large numbers of bioclastic microstructures with identical shapes and fine features (i.e., through sustained reproduction). Subsequent conversion reactions may then be used to simultaneously convert all of the microstructures into the desired ceramic composition while preserving the starting shapes and fine features (such conversion is illustrated with a color change in Figure 5).

While the feasibility of the BaSIC process has been demonstrated, further research is required to obtain better fundamental understanding and control of shape-dictating mechanisms during diatom biosilicification, and of the mechanisms of shape-preserving chemical conversion. Such research is the subject of a recently-awarded MURI proposal (“Genetically-Engineered Microdevices with Tailored 3-D Shapes, Nanoscale Features, and Chemistries,” K. H. Sandhage,

M. M. Hildebrand, B. P. Palenik, R. R. Naik, M. O. Stone, R. A. Rapp, A. T. Conlisk, Jr., D. J. Hansford) involving a multidisciplinary team with expertise in diatom microbiology, diatom genetics, biochemistry, and shape-preserving reaction processes.

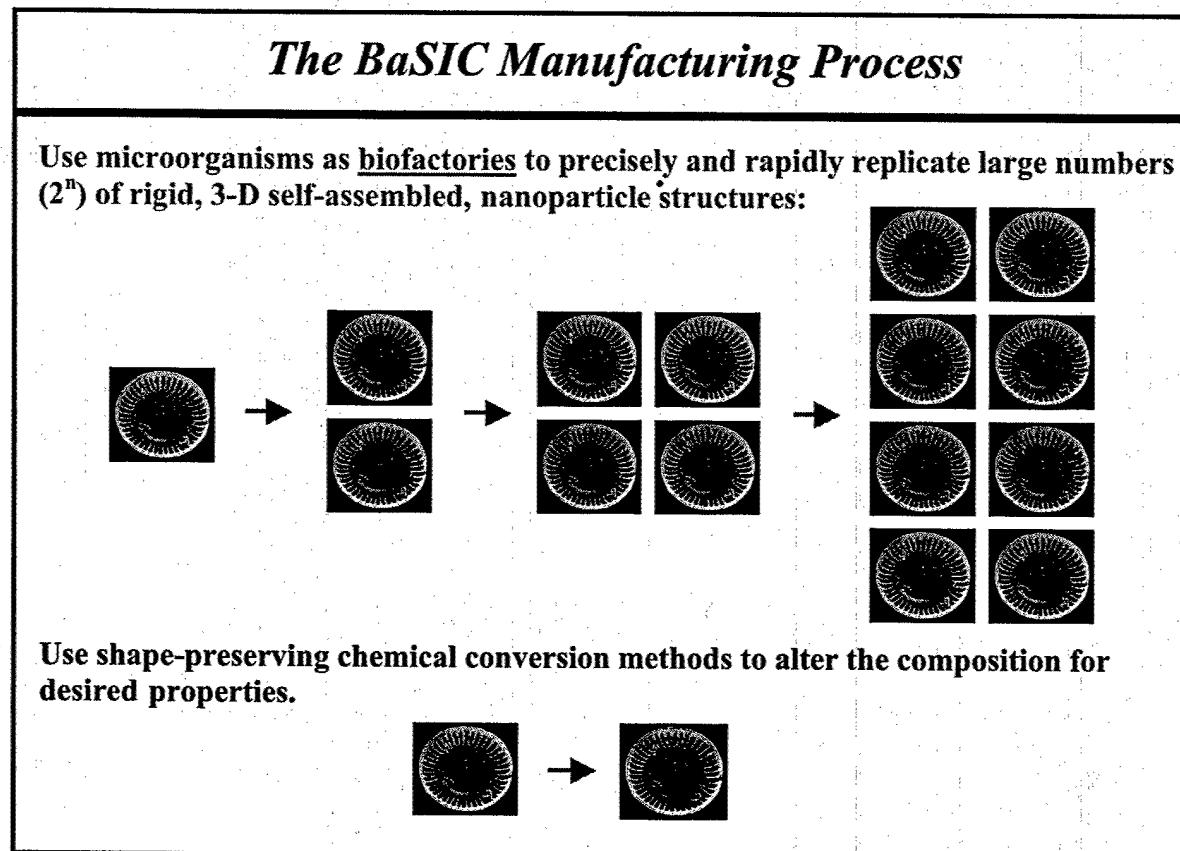


Figure 5. Schematic of the BaSIC process for mass producing 3-D ceramic microcomponents with tailored shapes, fine (meso-to-nanoscale) features, and chemistries.

Given the precision with which frustule shapes are replicated upon reproduction of a particular diatom species, it is apparent that such fidelity is under genetic control. Furthermore, given the wide variety of shapes exhibited by extant diatom species, it also appears that extensive alteration of the genes controlling the frustule shape is possible in viable diatoms. Hence, it is likely that genetic engineering of viable diatoms will lead to frustules with tailored (non-natural) shapes and nanoscale features. *Genetically-Engineered Micro/nanodevices (GEMs)* with tailored structures and compositions could then be mass produced by sustained reproduction of genetically-altered, viable diatoms followed by chemical conversion via the BaSIC process. Such BaSIC-derived micro/nanostructures with tailored shapes, features, and compositions could find widespread use in medicine (e.g., for targeted radiation or drug delivery), telecommunications (e.g., microoptical devices), transportation (e.g., microfluidic devices), manufacturing (e.g., microelectromechanical devices), energy production and storage (e.g., microfuel cells, microbatteries), and defense-based applications (e.g., microsensors, microtags).

# High-Temperature Residual Stresses in Textured Oxide Composites

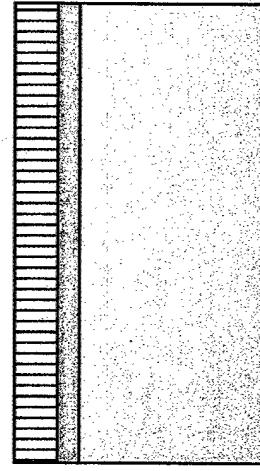
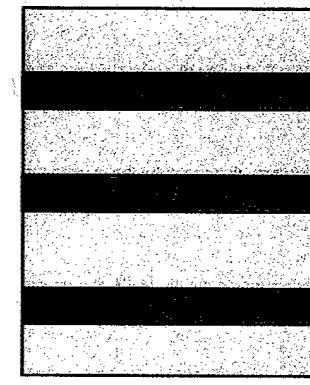
Elizabeth C. Dickey and Colleen Frazer  
Department of Materials Science and Engineering  
Materials Research Institute  
Pennsylvania State University

*AFOSR Grant F49620-02-1-0211*

*January 28, 2003*

## Motivation

- Many ceramic composites are textured
- Thermal residual stresses arising from mismatches in thermal expansion properties affects mechanical behavior and degradation



## Ceramic Matrix Composites

## Environmental Coatings

## Objectives

To understand the residual stress state of ceramic composites as a function of temperature and implications for mechanical behavior and degradation.

## Approach

Develop experimental techniques based on x-ray diffraction that facilitate residual stress measurement as a function of temperature.

## Outline

---

### I. Material Systems Studied: Directionally Solidified Oxide Eutectics (DSEs)

$\text{Al}_2\text{O}_3$ -YAG

$\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$ ( $\text{Y}_2\text{O}_3$ ) DSEs

-microstructure and crystallography

### II. Measuring Residual Stresses in Highly-Textured Materials

Measurement of strain tensor

Conversion to stress tensor

### III. Room Temperature Residual Stresses in DSEs

### IV. High Temperature Residual Stresses

### V. Conclusions

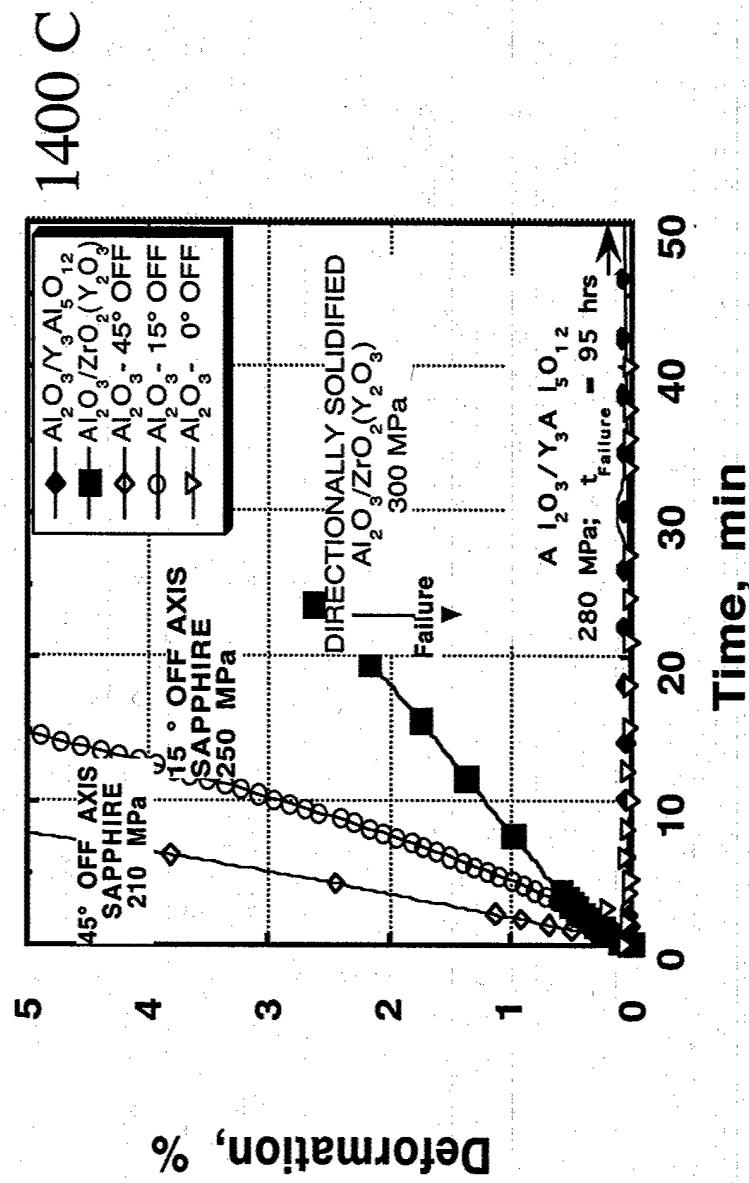
## Eutectic Systems

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Material	$\alpha_{11}$ (*10 <sup>-6</sup> C <sup>-1</sup> )	$\alpha_{33}$ (*10 <sup>-6</sup> C <sup>-1</sup> )
$\text{Al}_2\text{O}_3$	9.1	9.9
$\text{ZrO}_2$	14	
YAG		8.9

Directionally solidified oxide eutectics have excellent high-temperature strength and creep resistance

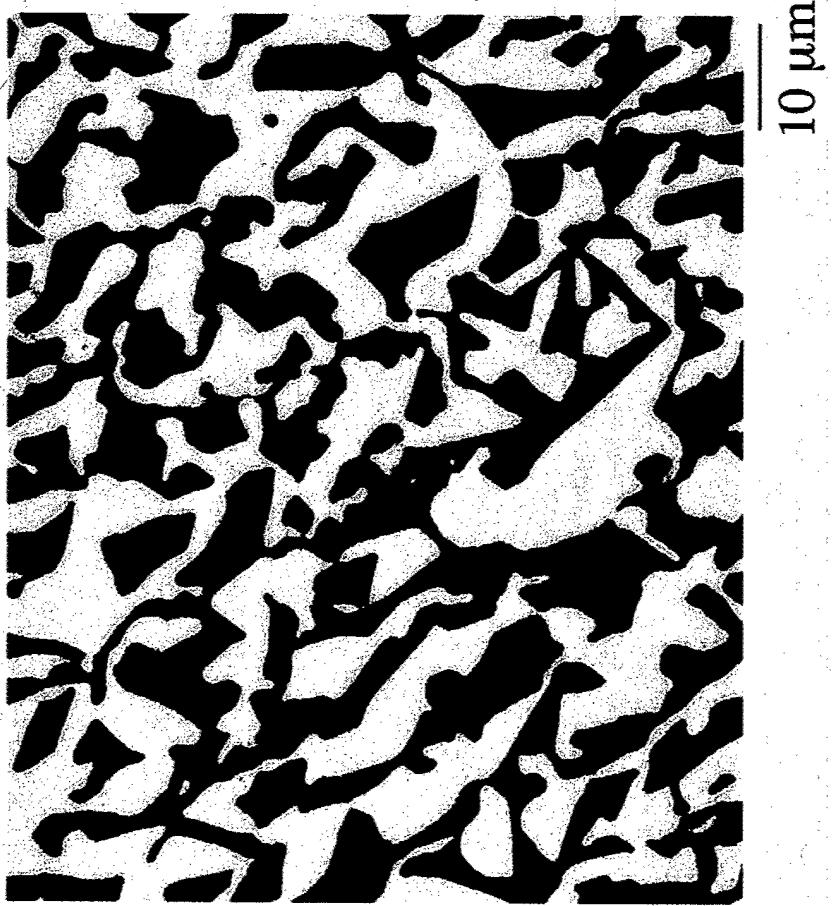


## Summary of Mechanical Behavior

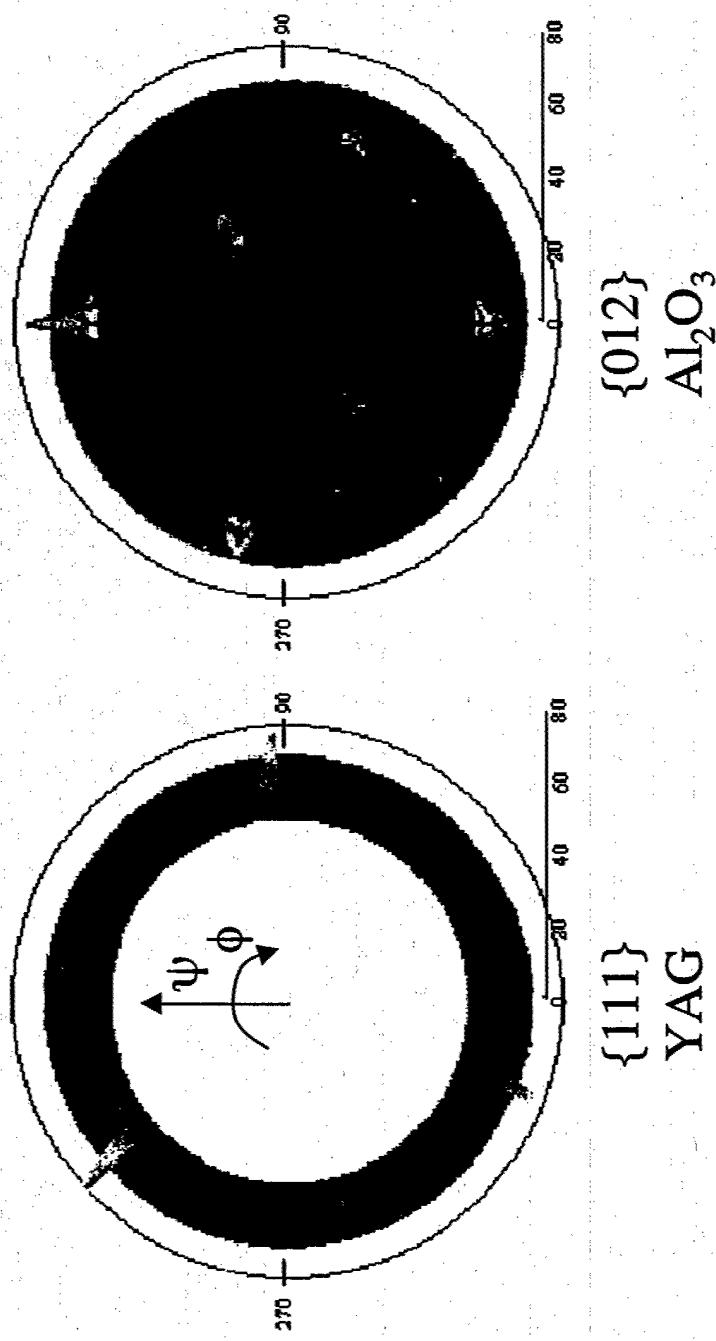
### (DSE) Composites

- » Better mechanical properties than either single phase
- » Tensile strength ~1 GPa for  $3.2\text{-}7.6\text{ m/o } \text{Y}_2\text{O}_3$
- » Strength maintained at elevated temperatures
- » Creep resistance
- »  $\sim 1.8 \times 10^{-5}/\text{s}$  at  $1400\text{ C }$  -  $\text{Al}_2\text{O}_3\text{-ZrO}_2$
- » Inherent oxidation resistance

# Al<sub>2</sub>O<sub>3</sub>-YAG DSES



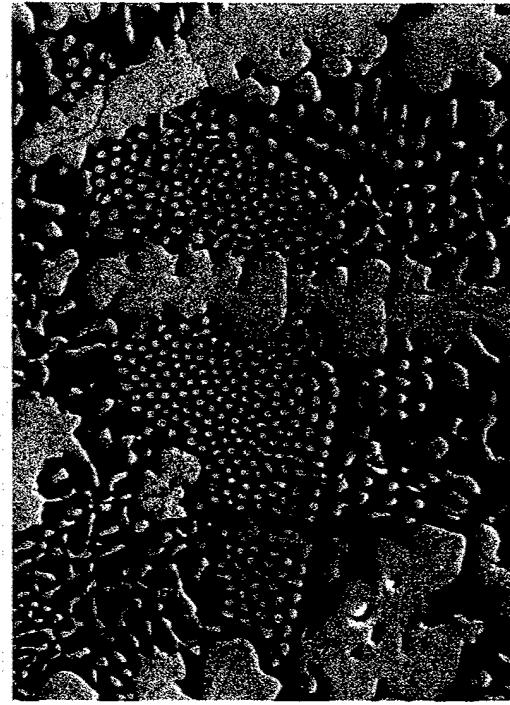
# X-ray Diffraction Pole Figures Show the $\text{Al}_2\text{O}_3$ -YAG DSEs to be Highly Textured



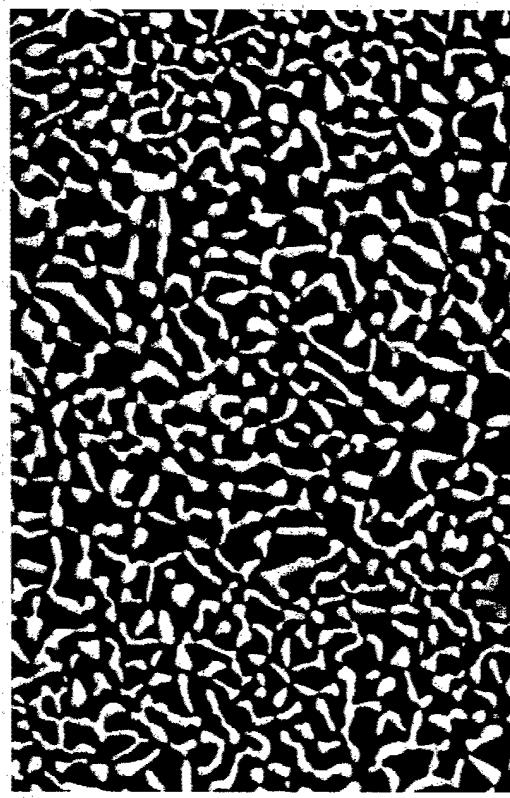
$[\bar{1}\bar{1}1]_{\text{YAG}} // [\bar{1}2\bar{1}]_{\text{Al}_2\text{O}_3} //$  growth direction  
 $(2\bar{1}1)_{\text{YAG}} // (111)_{\text{Al}_2\text{O}_3}$

## Eutectic Microstructure

---

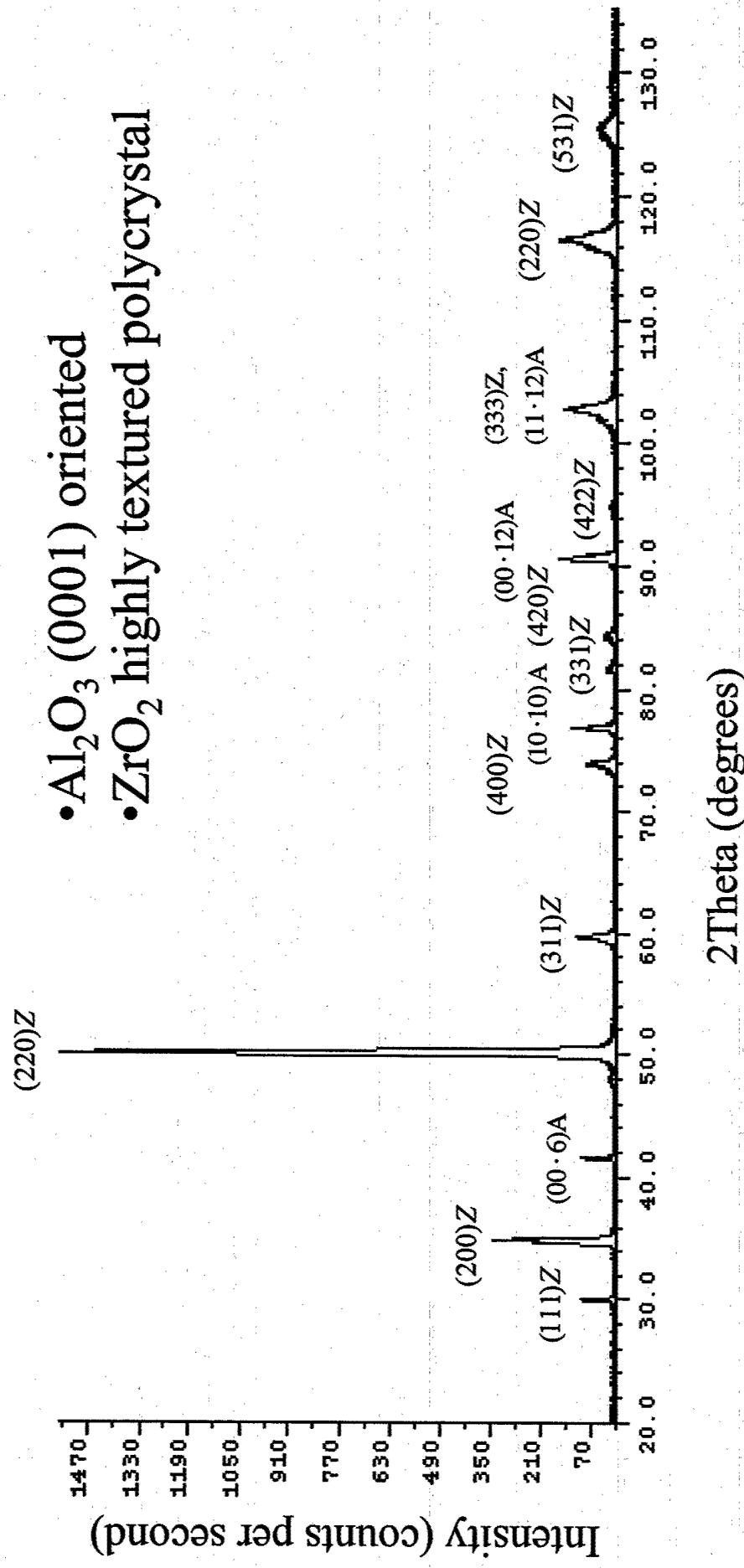


$\text{Al}_2\text{O}_3\text{-ZrO}_2\text{ (6.7\% Y}_2\text{O}_3\text{)}$

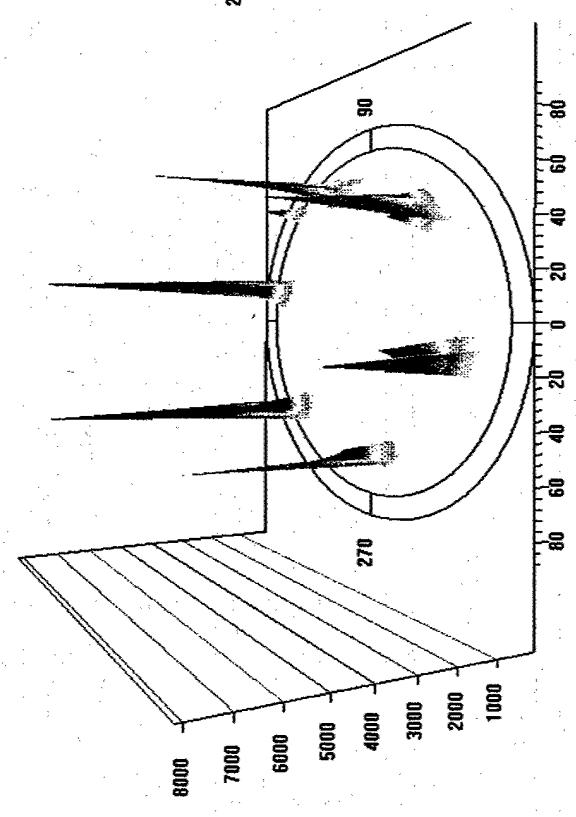


$\text{Al}_2\text{O}_3\text{-ZrO}_2\text{ (3.6\% Y}_2\text{O}_3\text{)}$

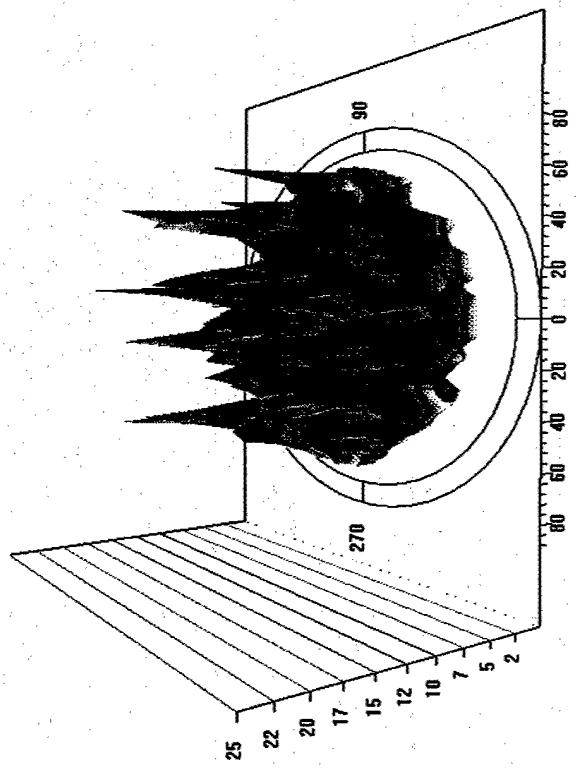
# X-Ray Diffraction Pattern of $\text{Al}_2\text{O}_3$ -cubic $\text{ZrO}_2$ Eutectic



# Crystallographic Texture Quantified from Pole Figure Analysis



(1123)  $\text{Al}_2\text{O}_3$  pole figure



(311)  $\text{ZrO}_2$  pole figure

Predominant Orientation  $[0001]\text{Al}_2\text{O}_3/[110]\text{ZrO}_2/\text{growth axis}$

## Outline

---

### I. Material Systems Studied

Al<sub>2</sub>O<sub>3</sub>-YAG

Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) DSEs

-microstructure and crystallography

### II. Measuring Residual Stresses in Highly-Textured Materials

### III. Room Temperature Residual Stresses in DSEs

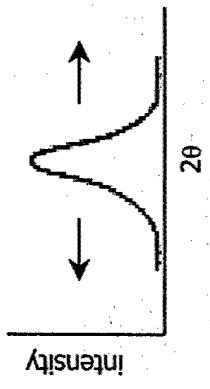
### IV. High Temperature Residual Stresses

### V. Conclusions

## Residual Stress Analysis

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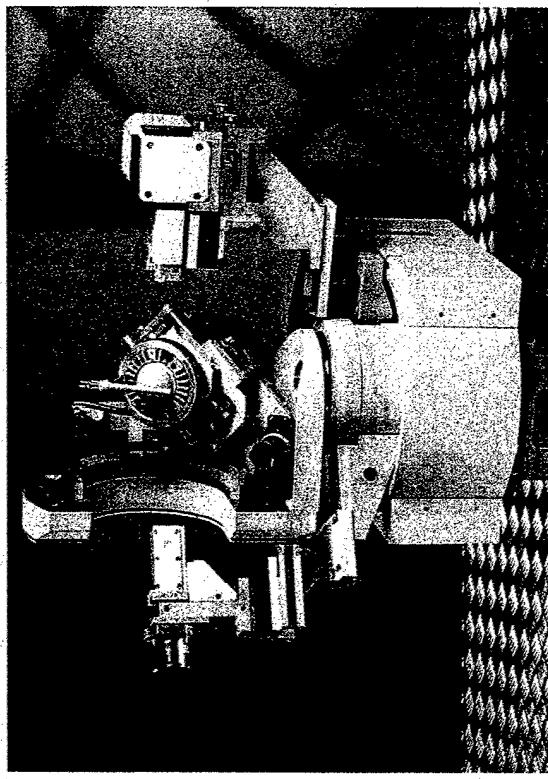
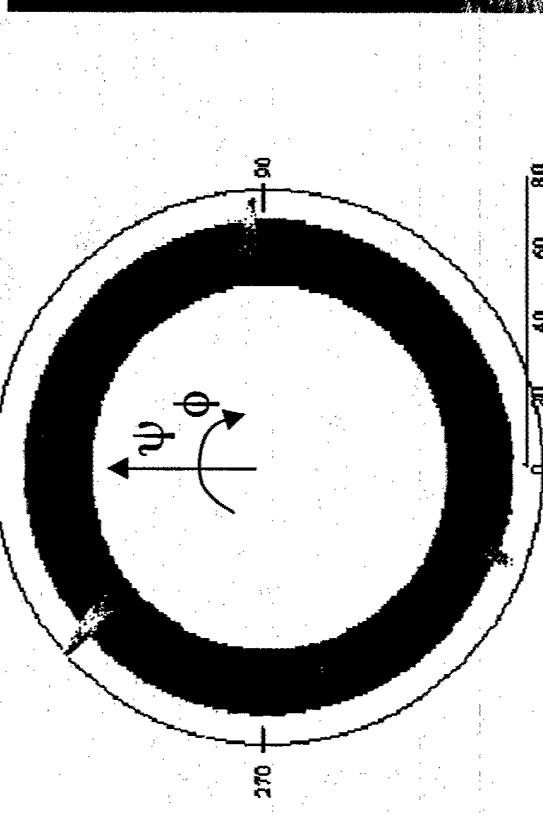
- Sample rotated to several different orientations ( $\psi, \phi$ )
- $d$  values measured from  $\theta-2\theta$  scans
- $d_0$  values measured from unstressed powders
- $\varepsilon$  values calculated for all sample orientations ( $\varepsilon_{\phi, \psi}$ )
- $\varepsilon$  and error values fit to x-ray strain equation using SVD least squares regression



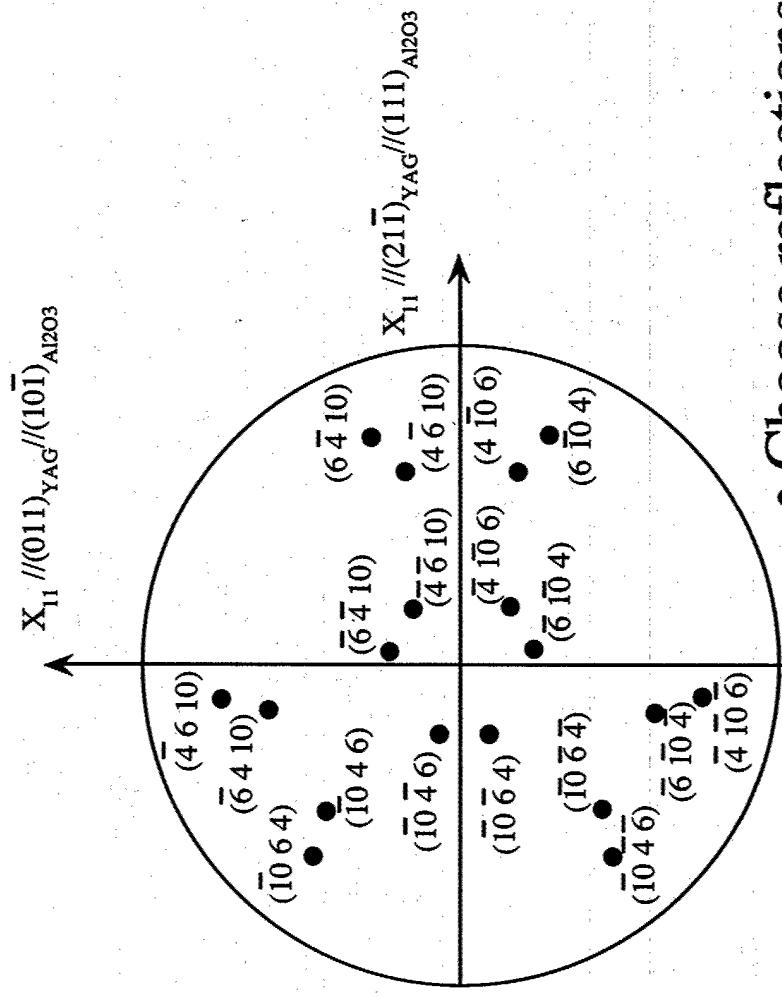
### Fundamental Equation of X-ray Strain Determination

$$\varepsilon_{\phi, \psi} = \frac{d_{\phi, \psi} - d_0}{d_0} = \varepsilon_{11} \cos^2 \phi \sin^2 \psi + \varepsilon_{22} \sin^2 \phi \sin^2 \psi + \varepsilon_{33} \cos \psi + \varepsilon_{13} \cos \phi \sin 2\psi + \varepsilon_{23} \sin \phi \sin 2\psi$$

# Parallel-Beam Optics on a Four-Circle Goniometer XRD Required for Stress Measurements

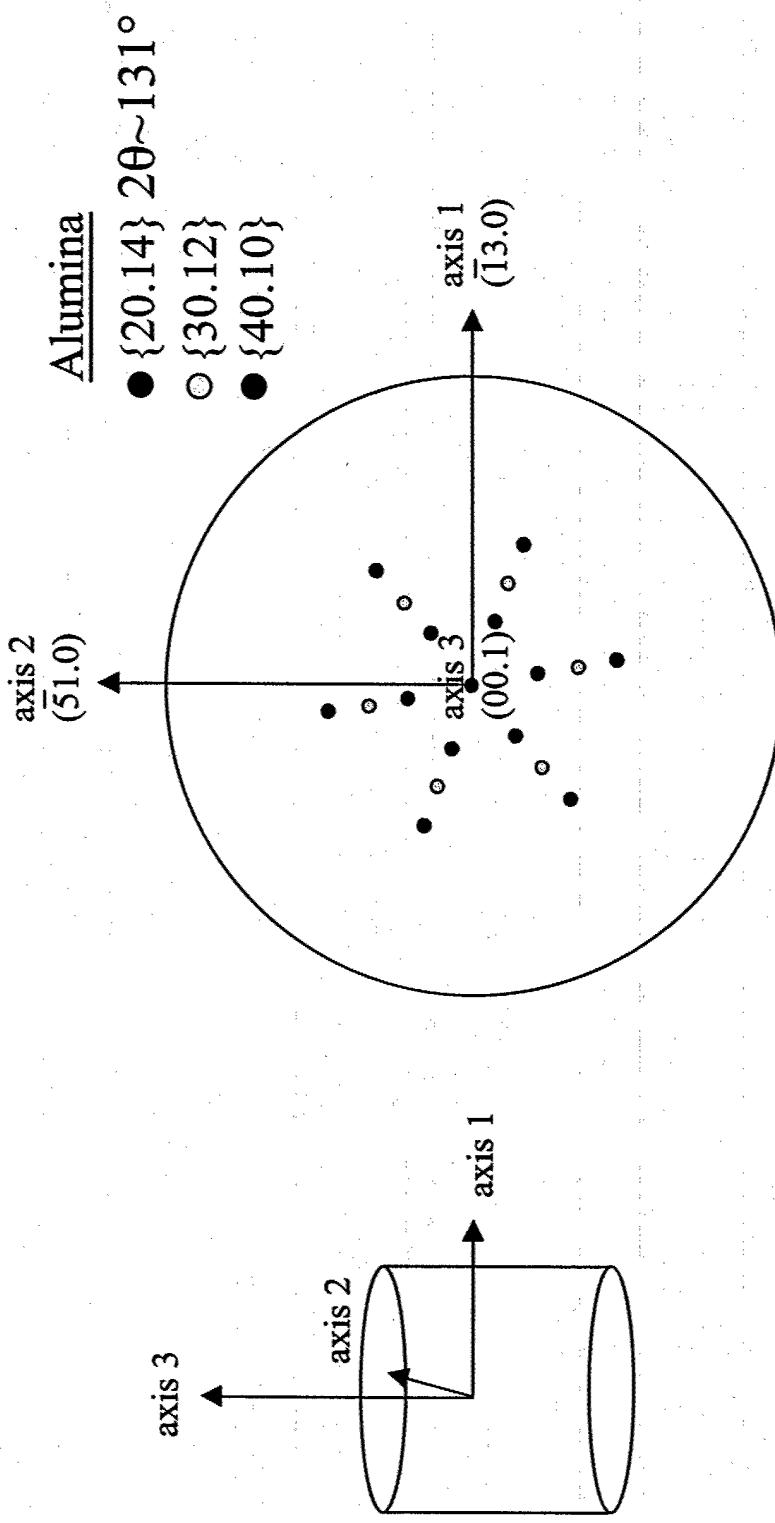


## Choice of Reflections Used for Strain Analysis e.g. YAG



- Choose reflections that have high scattering angles (better angular resolution)
- Choose reflections that have a high multiplicity

## Choice of Reflections Used for Strain Analysis e.g. $\text{Al}_2\text{O}_3$



## Conversion to Stress Tensor

$$\sigma_{ij} = C'_{ijk} \epsilon_{kl}$$

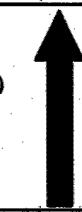
For single crystal:  
rotate stiffness tensor to correct reference frame

For highly textured:  
weight stiffness tensor with orientation distribution function

# Weighting Stiffness Matrix with Orientation Distribution Function

- Weighted stiffness tensor found

- 3 pole figures measured: (311), (111), (220)
- ODF calculated using Harmonic Coefficients (popLA)
- Produced weighted file of Euler angle orientations
- Used single crystal stiffness tensor as input file

$$[C]_{ij} \text{ (MPa)} \quad \begin{array}{|c|c|c|c|c|c|} \hline & 406 & 105 & 105 & 0 & 0 & 0 \\ \hline 105 & 406 & 105 & 0 & 0 & 0 & 0 \\ \hline 105 & 105 & 406 & 0 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 55 & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & 55 & 0 & 0 \\ \hline 0 & 0 & 0 & 0 & 0 & 55 & 0 \\ \hline \end{array} \quad + \text{weights} \quad \begin{array}{|c|c|c|c|c|c|} \hline & 336 & 140 & 140 & 2 & -1 & 2 \\ \hline 140 & 334 & 141 & 141 & 1 & 0 & 1 \\ \hline 140 & 141 & 334 & 0 & 1 & 1 & 1 \\ \hline -2 & 1 & 0 & 91 & 1 & -1 & 0 \\ \hline -1 & 0 & 1 & -1 & 1 & 0 & 2 \\ \hline 2 & -1 & -1 & 90 & 2 & 2 & 90 \\ \hline \end{array}$$


## Outline

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### I. Material Systems Studied

Al<sub>2</sub>O<sub>3</sub>-YAG

Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) DSEs

-microstructure and crystallography

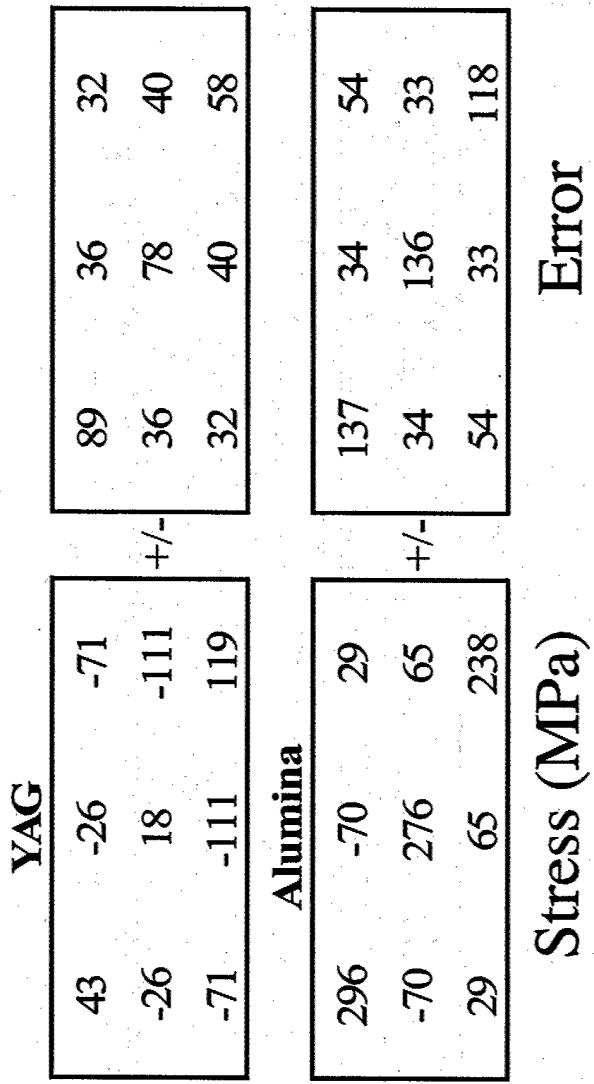
### II. Measuring Residual Stresses in Highly-Textured Materials

### III. Room Temperature Residual Stresses in DSEs

### IV. High Temperature Residual Stresses

### V. Conclusions

# Room Temperature Stresses in $\text{Al}_2\text{O}_3$ -YAG



18 YAG measurements on  $\{10\bar{6}4\}$

11 Alumina measurements on  $\{420\}\{532\}\{22\bar{2}\}$

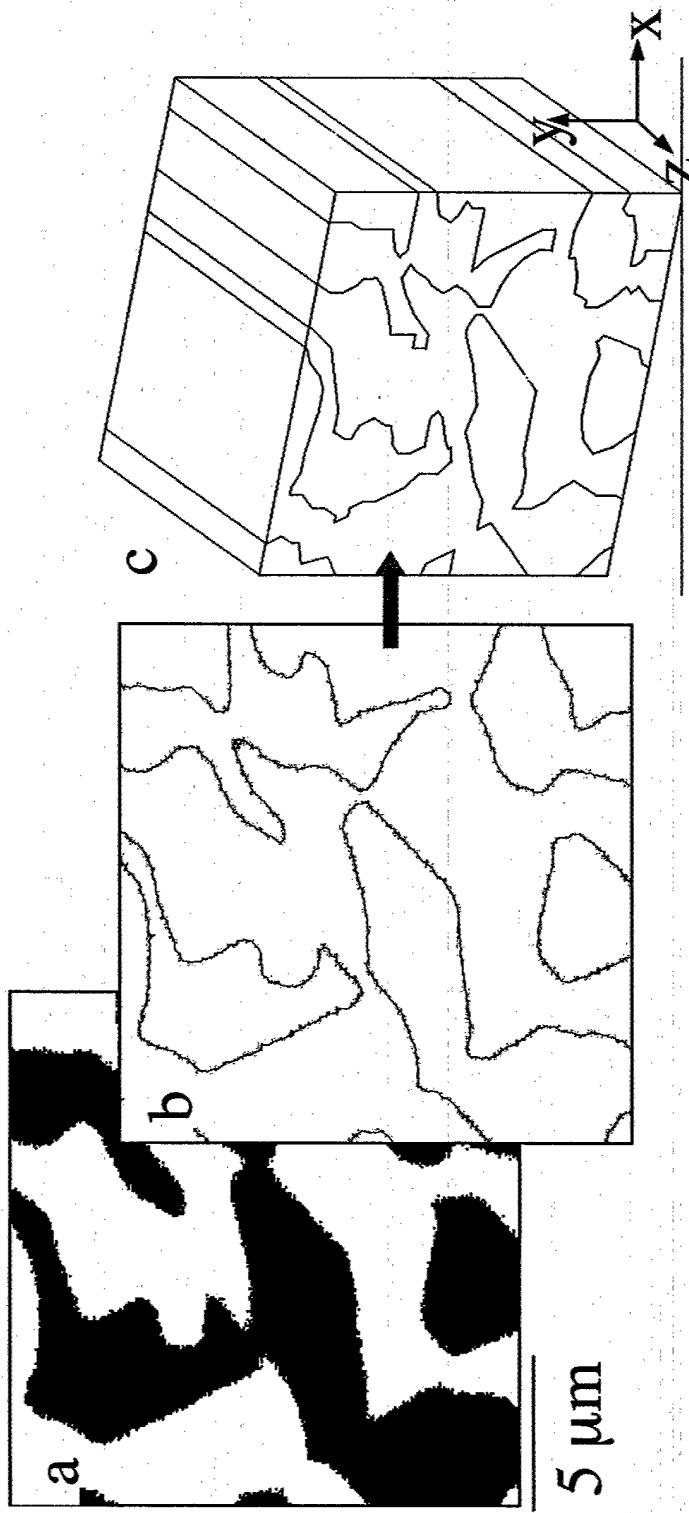
## Finite Element Modeling

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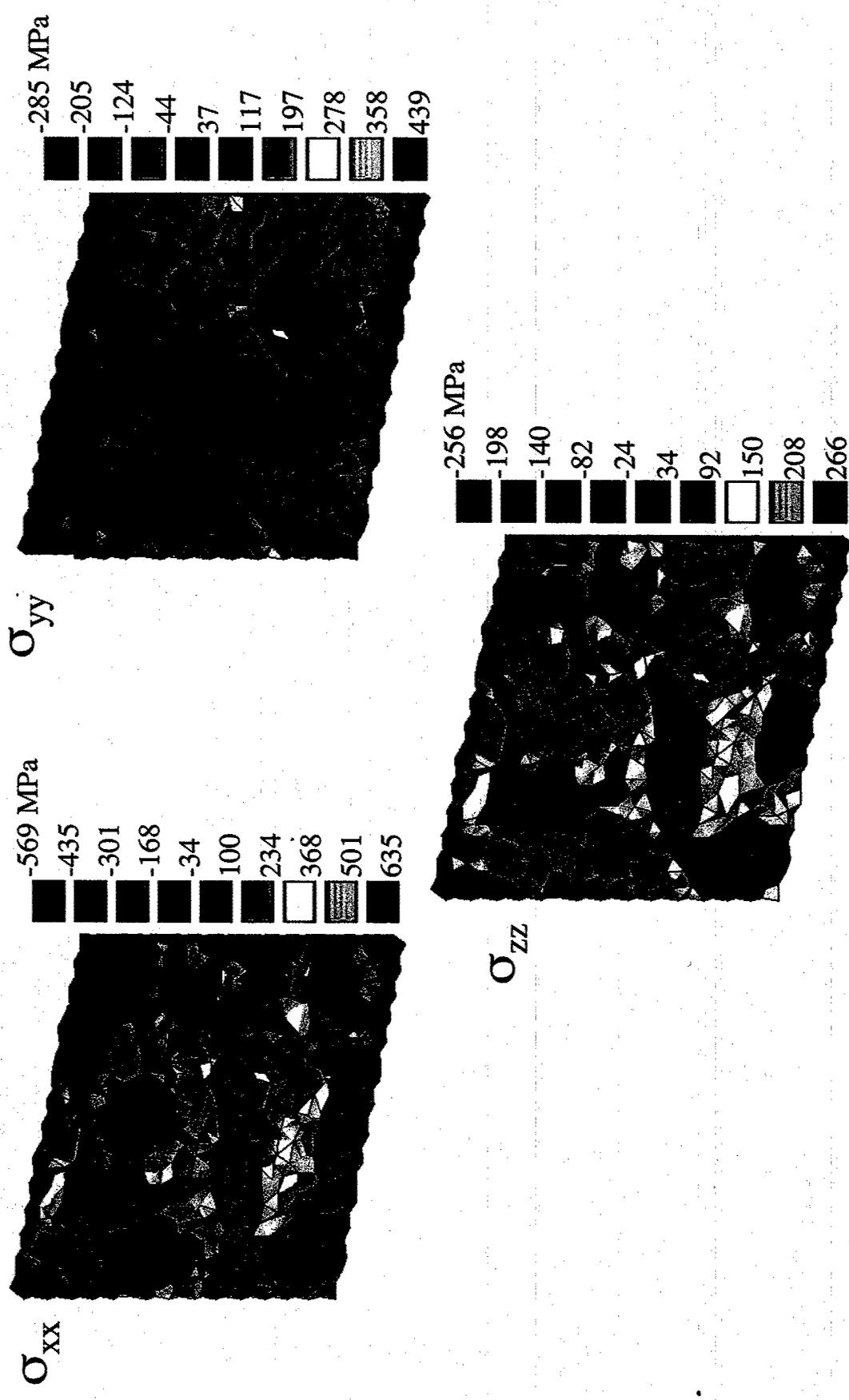
- Microstructure
- Crystallography

## Finite Element Modeling

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# Stress Concentrations Observed in FEM of YAG-Al<sub>2</sub>O<sub>3</sub>

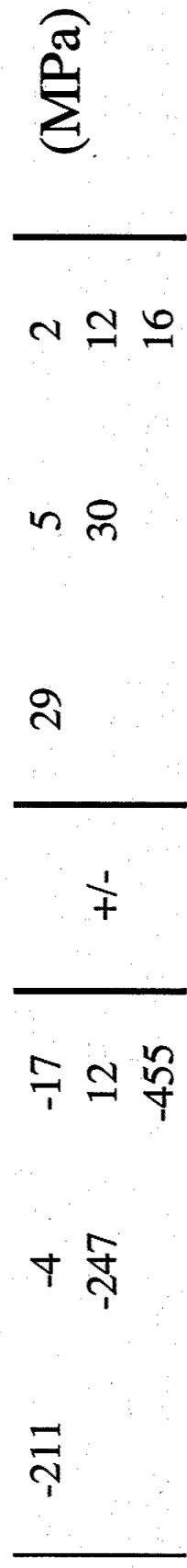


# Alumina-ZrO<sub>2</sub> Room Temp. Residual Stresses

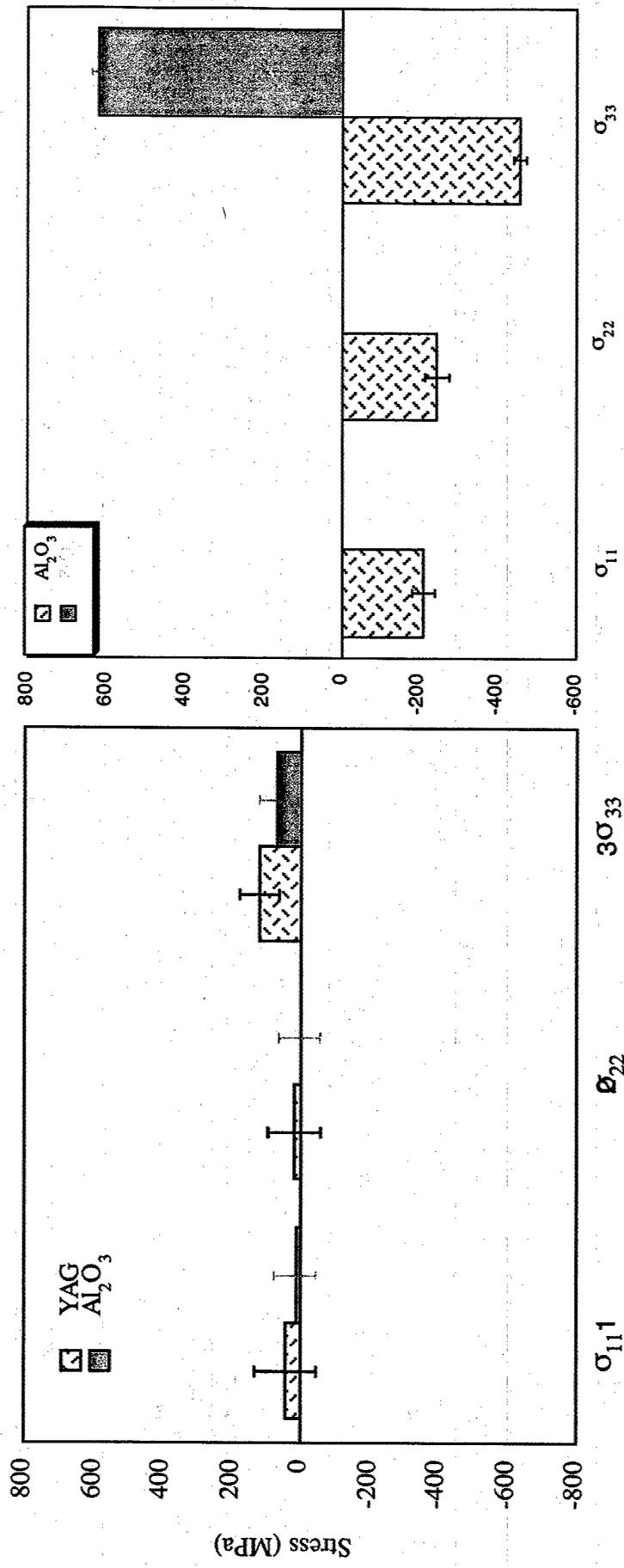
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Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> (3.6% Y<sub>2</sub>O<sub>3</sub>)

Al<sub>2</sub>O<sub>3</sub>:



# Comparison of Residual Stresses in Different Material Systems



## Outline

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### I. Material Systems Studied

$\text{Al}_2\text{O}_3$ -YAG

$\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$ ( $\text{Y}_2\text{O}_3$ ) DSes

-microstructure and crystallography

### II. Measuring Residual Stresses in Highly-Textured Materials

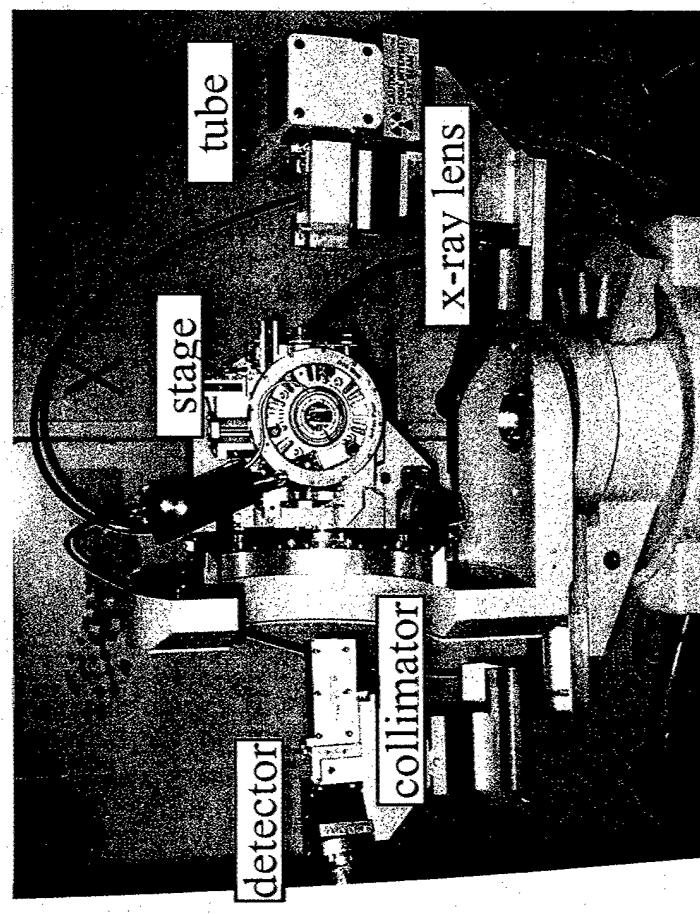
### III. Room Temperature Residual Stresses in DSes

### IV. High Temperature Residual Stresses

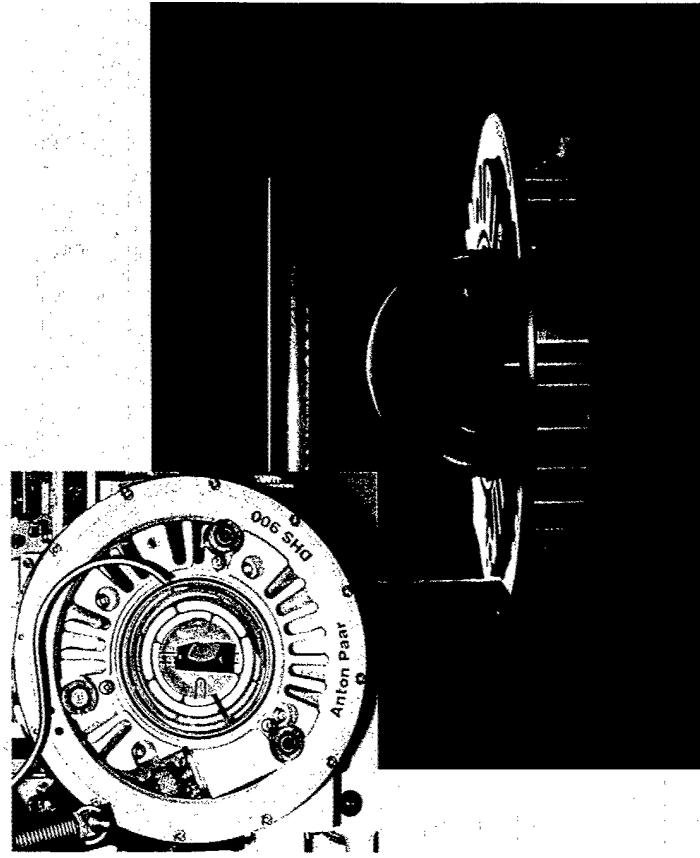
### V. Conclusions

## High-temperature X-ray Diffraction

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4-Circle Goniometer



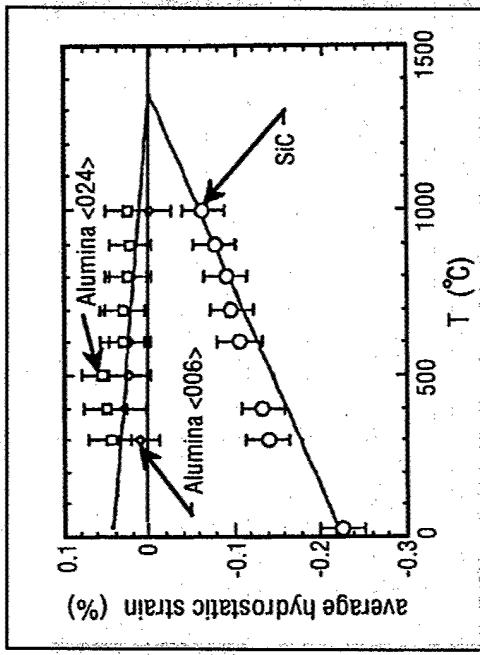
Anton Paar DHS 900 Domed Hot Stage

-Domed furnace capable of 900°C  
-air, vacuum, inert gas

## Temperature Effects on Residual Strain and Stress

### Temperature effects:

- thermal expansion
- stress-relieving mechanisms



stress relief due to elevated temperature

$$\varepsilon_{\phi\psi}(T) = \frac{d_{\phi\psi}(T) - d_0(T)}{d_0(T)}$$

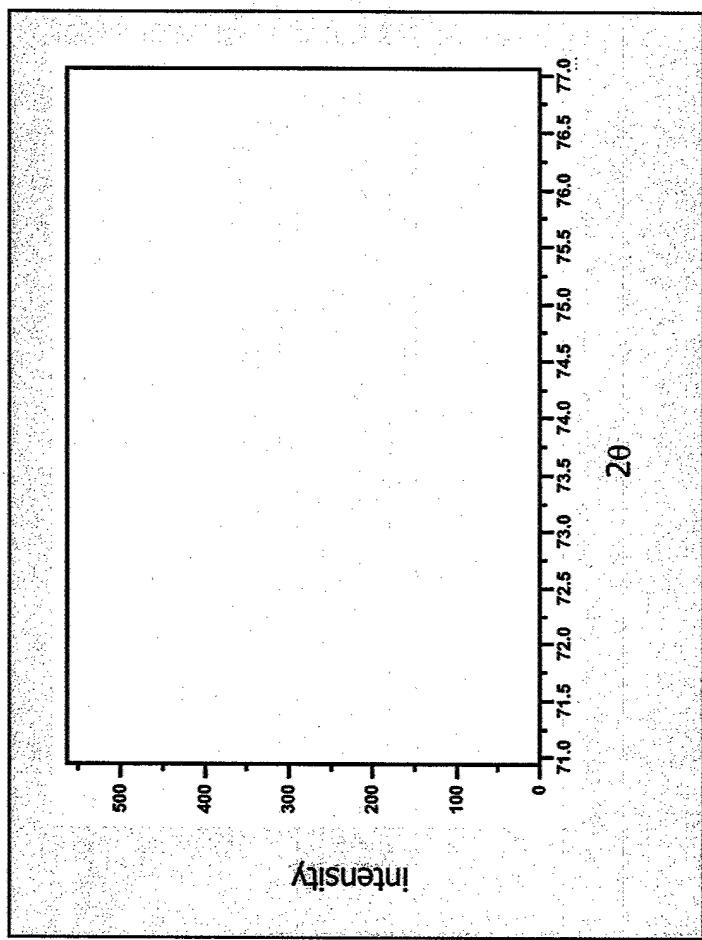
$$\downarrow \varepsilon_{kl}(T)$$

$$\downarrow$$

$$\sigma_{ij}(T) = C'_{ijkl}(T) \varepsilon_{kl}(T)$$

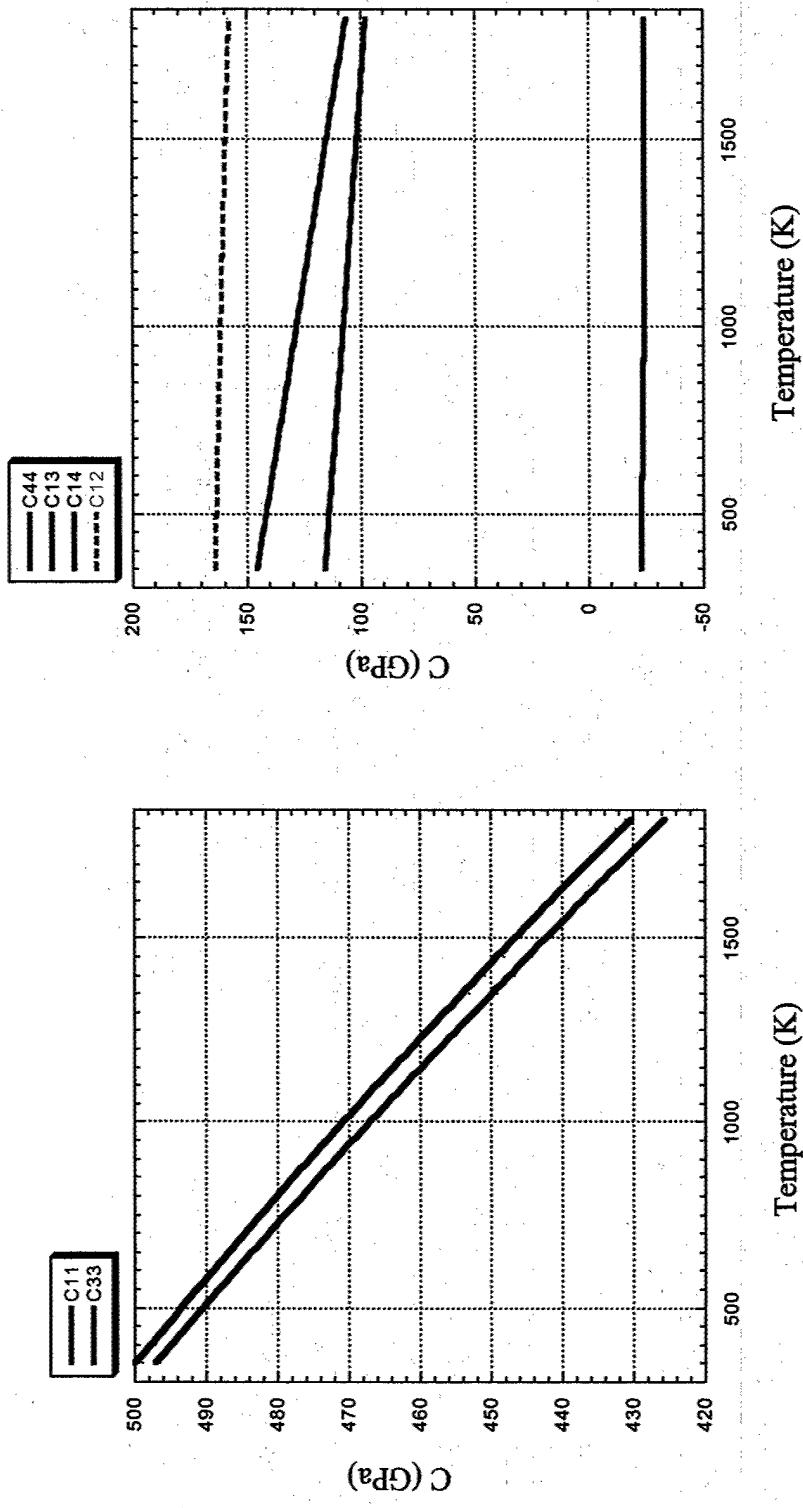
# Thermal Expansion Calibrated from Powder Samples

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peak shift due to thermal expansion

# Variation in Alumina Stiffness Tensor with Temperature



\*Goto, T. and O. L. Anderson, "Elastic Constants of Corundum Up To 1825 K", Journal of Geophysical Research, [94] 7588-7602 (1989)

[C <sub>ij</sub> ]		25°C					
		495	160	115	-19	12	0
160	495	115	115	19	-12	0	
115	115	497	0	146	0	0	(GPa)
-19	19	0	0	0	146	-19	
12	-12	0	0	-12	-19	167	
0	0	0					

[C <sub>ij</sub> ]		450°C					
		480	163	111	-20	13	0
163	480	111	111	20	-13	0	
111	111	484	0	0	0	0	(GPa)
-20	20	0	136	0	0	-13	
13	-13	0	0	0	136	-20	
0	0	0	-13	-20	20	158	

[C <sub>ij</sub> ]		900°C					
		459	161	106	-20	13	0
161	459	106	106	20	-13	0	
106	106	463	0	0	0	0	(GPa)
-20	20	0	124	0	0	-13	
13	-13	0	0	124	-20	-20	
0	0	0	-13	-20	20	149	

a)

b)

c)

# High-Temperature Stresses in $\text{Al}_2\text{O}_3\text{-ZrO}_2$ (3.6% $\text{Y}_2\text{O}_3$ )

a)  $[\sigma_{ij}]$  25°C

-211	-4	-17	29	5	2	12	16
-247	12	+/-					
-455							

b)  $[\sigma_{ij}]$  450°C

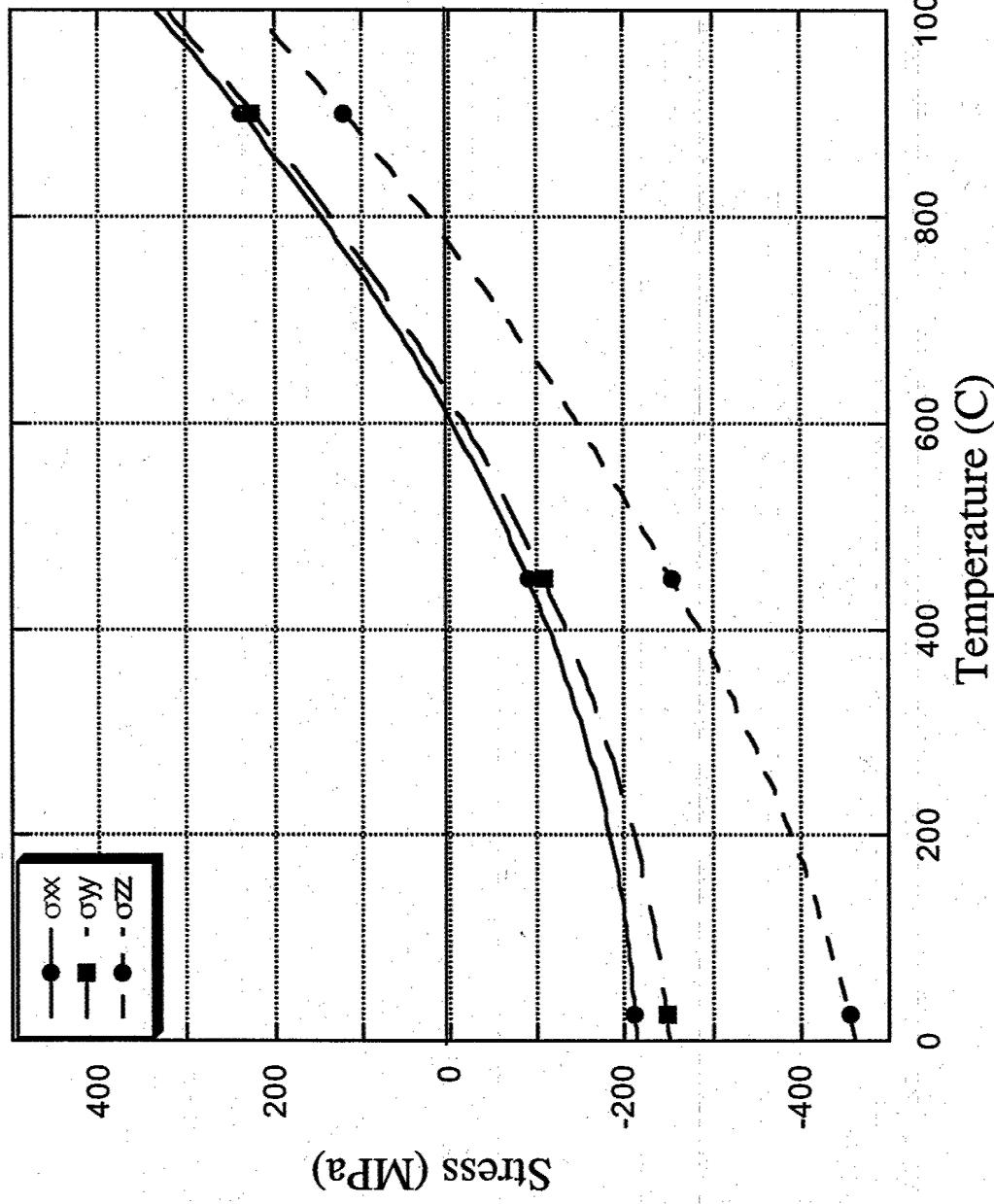
-89	3	-12	40	6	3	15	22
-107	9	+/-					
-253							

c)  $[\sigma_{ij}]$  900°C

236	2	-8	+/-	39	6	3	14
224	7			39			
		120					

## Stress-Free Temperature Determined

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## Summary

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- Developed a protocol for measuring residual stresses in highly textured composites
- Achieved successful operation of high-temperature 4-circle goniometer XRD
- Residual stresses are relatively insignificant in the  $\text{Al}_2\text{O}_3$ -YAG DSE
- Residual Stresses in  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$ ( $\text{Y}_2\text{O}_3$ ) DSE measured from RT-900°C
- Stress-free temperature determined to be 600-800°C
- Using finite element modeling to help interpret x-ray diffraction data and to understand stress distributions in the microstructure

# MOLTEN SALTS: A ROUTE TO TAILORED CERAMICS

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## Formation of ceramics in molten salts

- ✓ Molten salt synthesis is a well established process of forming a desirable compound in a flux of low melting point.
- ✓ It offers a significant reduction in the formation temperature when compared to that required in a conventional solid state reaction, since the diffusivities of the reactants are accelerated.
- ✓ It also provides great control on the particle size and morphology of the resulting copowders.

The formation process of ceramic phase in a molten salt is complicated; ✓ in some cases, the molten salt reacts with the reactant to form an intermediate compound, which then decomposes to the required ceramic phase. For example, in the preparation of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  powders, the component oxides firstly react with  $\text{LiCl}$  flux to form an intermediate compound, which subsequently decomposes into  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  and  $\text{LiCl}$  [4].

- ✓ In other cases, the molten salt is acting as a mere reaction and diffusing medium accelerating the rate of formation of the desirable ceramic phase.

*T. Kirmura, T. Kanazawa, T. Yamaguchi  
J. Am. Ceram. Soc. 66(8) (1983) 597*

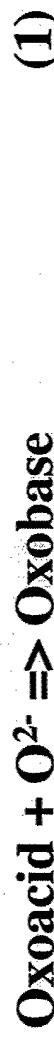
- The method consists of adding precursors in the required ratio to a molten salt mixture often close to an eutectic stoichiometry, which accelerates the kinetics of formation of the desired compounds. Molten salt mixtures either serve the role of a solvent with no direct participation in the reaction or may actually enter into reaction with the oxide additives.
- ✓ In cases where the molten salt serves merely as a solvent medium, its sole purpose is to accelerate the kinetics by enhancing diffusion, since coefficients in the liquid state are lower than those in the solid state.
- ✓ Reactions are presumed to occur by the dissolution of constituents, reaction of the constituents in solution, and precipitation of the required compounds upon exceeding the solubility limit.

- ❑ Molten salts as reaction media provide an alternative to aqueous chemistry by offering the possibility to change the solubility and/or the reactivity of the reactants, and to increase the reaction temperature
- ✓ used for the preparation of solids, recrystallization and growth.
- ✓ So far, attention in this field has been largely focused on the alkali and alkaline-earth halides and polychalcogenides. To grow anisotropic crystals,  $KCl-NaCl$  and  $K_2SO_4-Na_2SO_4$  fluxes have been used, as well as molybdates and tungstates.
- ✓ Alkali carbonate and alkali hydroxide fluxes have also been used for the preparation of various oxides.
- ✓ These oxosalts offer a wide range of reaction temperatures (see next Table) and a great variety of possible chemical reactions, including those of complexation, oxidation-reduction, and acid-base type reactions.

Melting points of some oxosalt mixtures (m.p.: melting point)

Molten salt	$\text{NaNO}_3\text{-KNO}_3$	$\text{Li}_2\text{CO}_3\text{-Na}_2\text{CO}_3$	$\text{Li}_2\text{SO}_4\text{-K}_2\text{SO}_4$	$\text{LiBO}_2\text{-KBO}_2$	$\text{Na}_2\text{SiO}_3\text{-K}_2\text{SiO}_3$
Composition (mole%)	50-50	50-50	71.6-28.4	56-44	18-82
M.p. (K)	501	773	808	855	1025

Acid-base type reactions occurring in molten oxosalts are classified as Lux-Flood (L-F) acid-base reactions, oxide donors and acceptors being defined as L-F bases and acids, respectively, and the reaction is understood as follows:

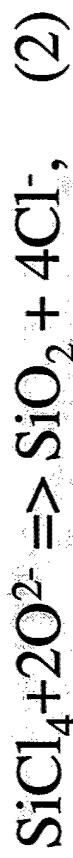


The basicity of the melt is usually expressed by

$$\text{pO}^{2-} = -\log m(\text{O}^{2-})$$

where  $\log m(\text{O}^{2-})$  corresponds to the concentration of  $\text{O}^{2-}$  ions. Depending on the reactant and basicity of the oxosalt, precipitation of an oxide or formation of an oxoanion can occur in the molten bath.

For example, the reaction of silicon tetrachloride with an oxosalt melt at moderate  $pO_2^-$  leads to precipitation of silica:



whereas if the melt basicity is further increased (low  $pO_2^-$ ), redissolution of  $SiO_2$  may occur, caused by formation of metasilicate:

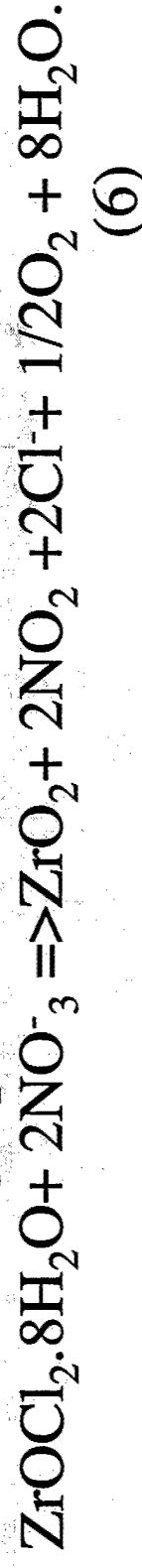


Then, depending on the nature of the molten salt, different species can be obtained and the nature of the products can be controlled.

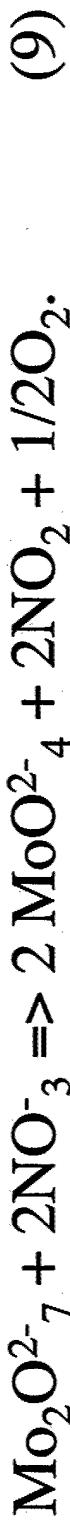
## The chemistry of molten nitrates



- zirconium oxide is obtained from zirconium(IV) salts according to the following equation:



- Soluble oxoanions can be produced from molybdenum oxide which undergoes stepwise transformations (Eqs. (3)–(6)), leading to alkali metal molybdates  $\text{A}_2\text{MoO}_4$  ( $\text{A}=\text{K, Na}$ ):



## Synthesis of solids in molten nitrates:

*Usually performed in a Pyrex glass reactor in air or under an inert atmosphere*

- ✓ Precursor salt(s) mixed with a large excess of the nitrate salt
- ✓ The most often used melts : equimolar  $\text{NaNO}_3$ - $\text{KNO}_3$  mixture ( $\text{mp}=501$  K), or individual alkali metal nitrates.
- ✓ Mixture pretreated at 423 K to eliminate water from the precursor salt(s) up to above  $T_{\text{fus}}$ .
- ✓ After cooling down, the solidified melt is thoroughly washed with distilled water to separate the (necessarily water-insoluble) solid product from the soluble salts.
- ✓ Then the product is dried in air at 393 K..
- ✓ For catalytic applications, the dried product is usually calcined in air at 683-773 K.

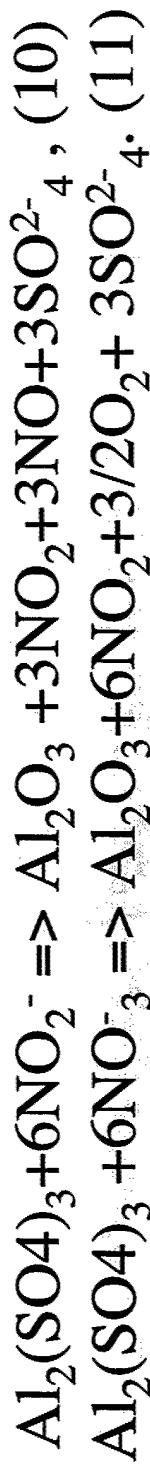
*P. Afanasiev, C. Geantet  
Coordination Chemistry Reviews, 178-180 (1998) 1725-1752*

## Zirconium oxide

*Several studies were devoted to the influence of the MS reaction conditions on the properties of zirconia obtained.*

- The nature of the cation of the alkali metal nitrate has a strong influence on the properties of the oxide, affecting the specific surface areas, as well as pore size distributions.
- It has been shown by transmission and scanning electron microscopies that the oxide obtained from molten nitrates has nearly spherical morphology, very different from that of aqueous precipitates, which are rough and irregular. It may be one of the reasons for its higher stability toward calcination. This parameter is important for catalytic applications.
- The influence of acidity/basicity of nitrate melt as also
- the effects of the starting materials of  $\alpha$ -Zr(SO<sub>4</sub>)<sub>2</sub> and  $\beta$ -Zr(SO<sub>4</sub>)<sub>2</sub>, on the phase composition and the crystallite size of zirconia powders prepared were investigated

## Aluminum oxide

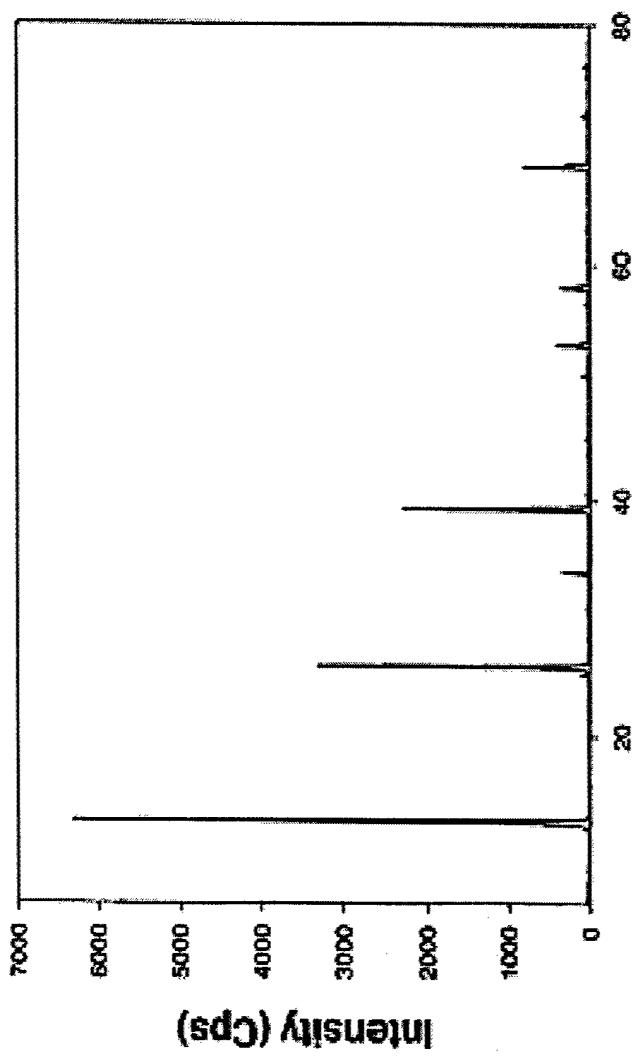
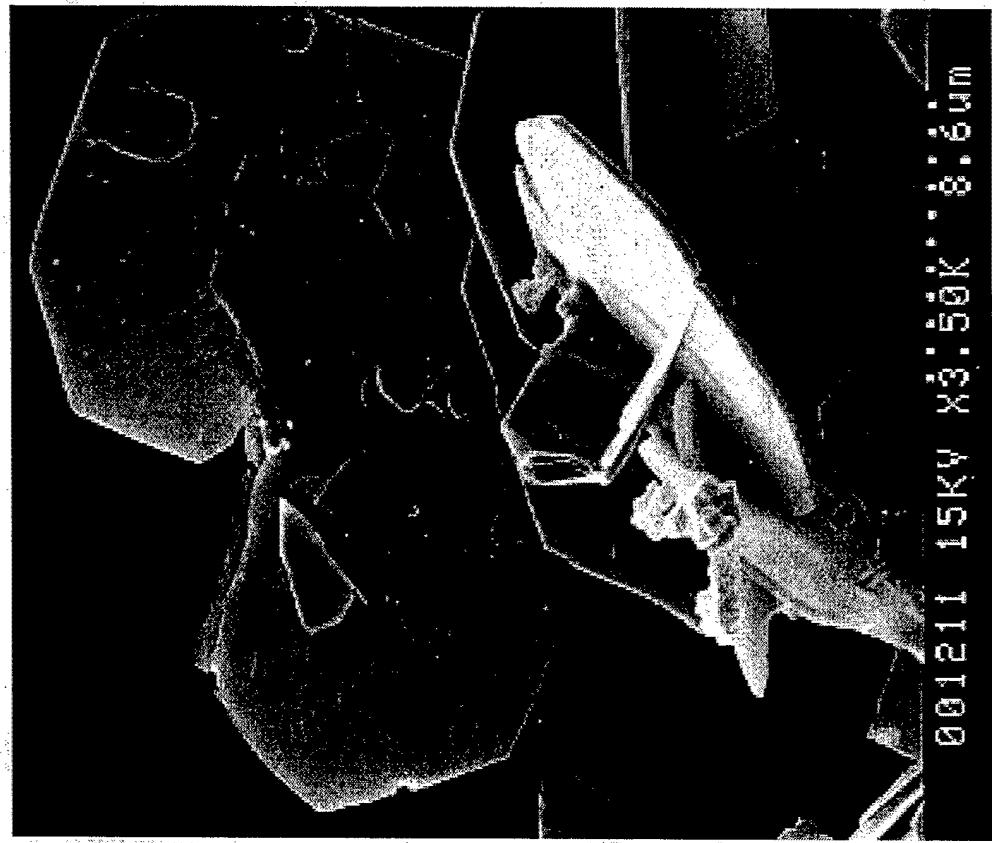


- The nature of the starting compounds is of primary importance in the case of aluminum.
- With highly reactive anhydrous salts : reaction at very low T ( to some extent already upon mixing), and  $\alpha$ -alumina formed.
- With hydrated Al(III) salts : much lower reactivity and quite different properties of the product, e.g. solid obtained hydrated Al(III) chloride or nitrate at 450–550 °C in molten NaNO<sub>3</sub>, KNO<sub>3</sub> or their mixture, was virtually amorphous. On contact with washing water it could easily be hydrated, forming crystalline Al(OH)<sub>3</sub> as Bayerite. Since the washing step leads to the chemical transformation of the product, the MS preparation for alumina from hydrated precursors seems rather useless.
- Moreover, though well-dispersed aluminium oxide could be prepared from molten nitrates, more simple precipitation routes give at least as good textural parameters as the MS technique.

## Lanthanum oxide

□ Since La (III) is a weak L-F acid, the reaction of  $\text{LaCl}_3$  occurs at high temperatures (above  $450^\circ\text{C}$ ). It is difficult to accomplish because the intermediate product  $\text{LaOCl}$  is poorly reactive and insoluble. Washing of the reaction product with water always leads to crystalline  $\text{La}(\text{OH})_3$  as in the case of alumina.

□ However, the reaction of  $\text{LaCl}_3$  seems to be of some interest since **pure  $\text{LaOCl}$  can be obtained at  $450\text{--}500^\circ\text{C}$  (Fig.).** Using the MS preparation, this compound possesses highly oriented sheet-like morphology, as can be seen from the scanning electron microscopy images. The oxychloride obtained by this method can be used as an **intercalation host**, or as a **reactive precursor** for further solid preparations.



**XRD pattern and SEM  
picture of LaOCl prepared  
in molten LiNO<sub>3</sub> at 773 K.**

P. Afanasiev, C. Geantet  
*Coordination Chemistry Reviews*, 178–180  
(1998) 1725–1752

001211 15K4 x3:50K x8:6um

## Synthesis of multicomponent oxide systems

*Most advanced materials for ceramics and catalysis are complex multicomponent systems, containing, for instance, solid solutions such as yttria-stabilised zirconia ceramics or fine dispersions i.e. mixed oxide catalytic supports on the base of alumina, doped with La, B, Ti etc.*

- Various methods developed to achieve the desired chemical composition and morphology of the multicomponent inorganic materials.
- Used for tailor-made preparations of solids with given properties, not available by classical solid preparation methods involving heating and grinding.
- The common feature of these methods is that the solid products keep some memory about the precursors and additives used during the preparation. Being carried out at relatively low temperatures, they often lead to metastable solids: homogeneous or heterogeneous nanodispersions; double hydroxides; or organic-inorganic hybrid materials.

## $\text{ZrO}_2\text{-Y}_2\text{O}_3$

• Solid solutions  $\text{ZrO}_2\text{-Y}_2\text{O}_3$  prepared in Ref. [a] by simultaneous reaction of zirconium oxychloride and yttrium chloride in  $\text{NaNO}_3\text{-KNO}_3$  melt at 450 °C.

• A tetragonal or cubic phase was obtained according to the yttrium content.  
• The large specific area of the powders was observed (up to 120 m<sup>2</sup> g<sup>-1</sup>), suggesting their possible application for ceramics or catalysis.

## $\text{ZrO}_2\text{-Al}_2\text{O}_3$

• by simultaneous reaction of hydrated  $\text{ZrOCl}_2$  and  $\text{AlCl}_3$  at 450 °C, using different nitrate melts [b, c].  
• The presence of alumina delays the growth of the zirconia particles, stabilising its tetragonal modification.

[a] M. Jebrouni, B. Durand, M. Roubin, *Ann. Chim. Fr.* 17 (1992) 143.

[b] M. Jebrouni, B. Durand, M. Roubin, Y. Saikali, *Ann. Chim. Fr.* 19 (1994) 55.

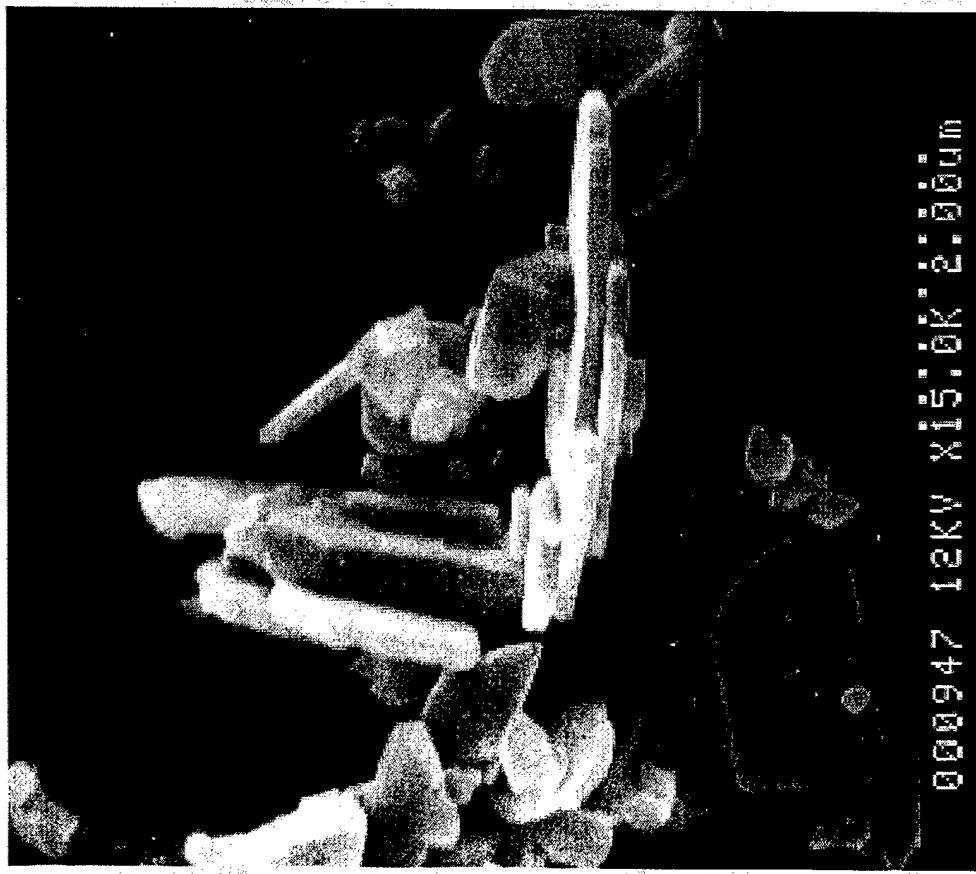
[c] D. Hamon, M. Vrinat, M. Breysse, B. Durand, L. Mosoni, M. Roubin, *T. des Courrières, Eur. J. Solid State Inorg. Chem.* 30 (1993) 713.

## Ternary oxides and oxosalts

*If one of the precursors precipitates an oxide and another provides an oxoanion soluble in the melt, the formation of ternary or more complex stoichiometric compounds is possible.*

- Molybdenum-based unsupported catalysts represent an important class of industrial oxidation catalysts and several transition-metal-doped molybdates were prepared including  $\text{NiMoO}_4$ ,  $\text{K}_3\text{FeMo}_4\text{O}_{15}$ ;  $\text{NaFe}(\text{MoO}_4)_2$ ;  $\text{Fe}_2(\text{MoO}_4)_2$ ;  $\text{NaCO}_{2.31}(\text{MoO}_4)_3$ ; and  $\text{CoMoO}_4$ .
- Bismuth molybdate is used as a catalyst for the production of acrylonitrile via ammoniation of propene (SOHIO process). A bismuth molybdate has been prepared in molten nitrates at 773 K from the simultaneous reactions of hydrated  $\text{Bi}(\text{NO}_3)_3$  and  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ .

The product corresponds to the  $\text{Bi}_2\text{MoO}_6$  phase,



P. Afanasiiev, C. Geantet  
*Coordination Chemistry Reviews*,  
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000947 12KV X15.0K 2.00μm

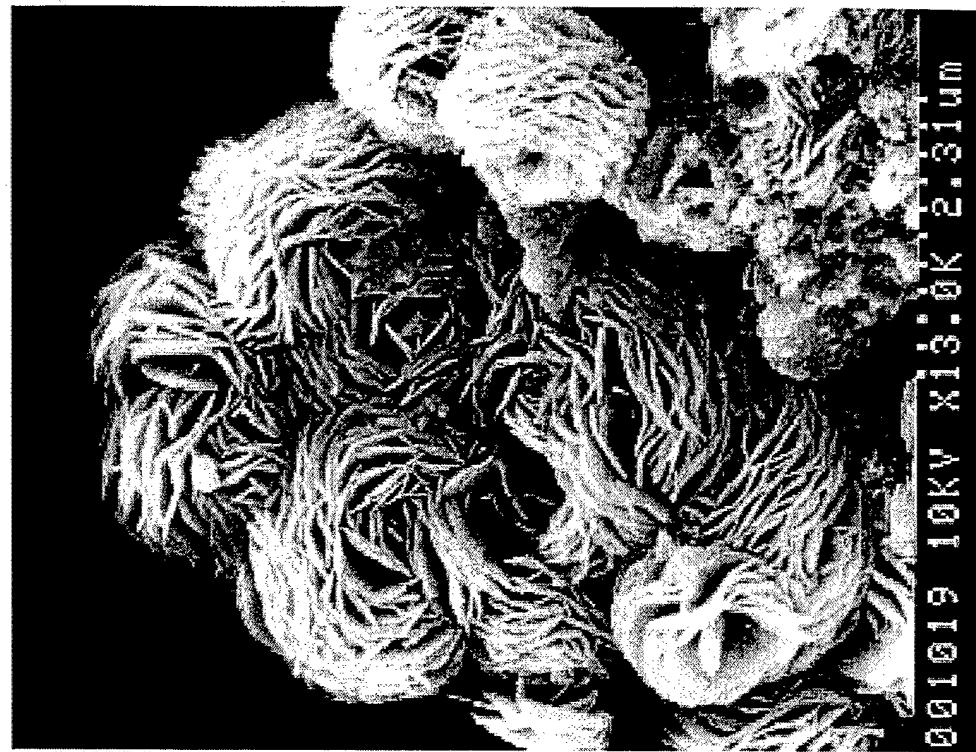
## Lamellar Zr\_Na sulphate

- It was reported earlier that the reaction of  $Zr(SO_4)_2$  in molten nitrate gives  $ZrO_2$  at 500 °C, but, due to the complexing properties of sulphate, the reaction is difficult to accomplish.
- It appears that an intermediate product of this reaction, which can be isolated at lower temperatures, presents independent interest as a new lamellar compound with ion-exchanging properties and the possibility to be intercalated with organic amines.
- The product (called NaZ) was obtained by reacting  $ZrOCl_2$  in molten  $NaNO_3-Na_2SO_4$  (molar ratio=4/1) melt at 673 K. The chemical composition of the product corresponds with the composition  $ZrS_{0.33}Na_{0.21}O_x$ .

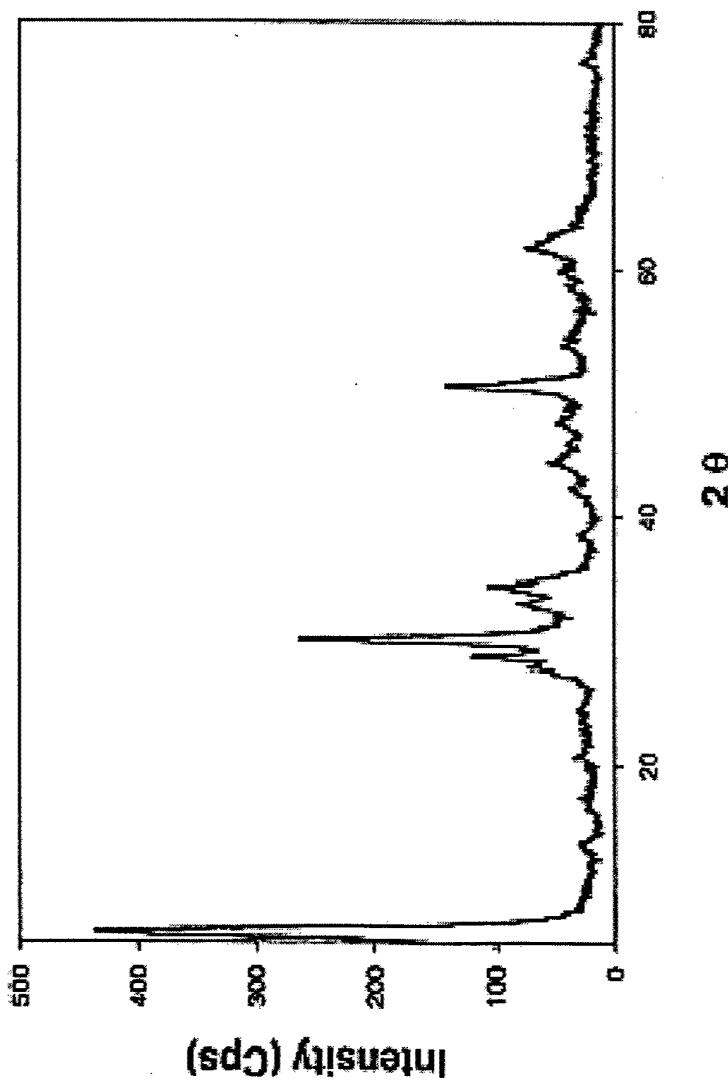
# Synthesis of lamellar Zr-Na sulphate: new ion exchanger and intercalation host



SEM picture of  
 $K_2Ni_4(P_2O_7)_2(PO_4)$   
prepared in molten  
 $KNO_3$  at 773 K.



001019 10KV x13.0K 2.31um



XRD pattern and SEM picture of  
NaZ compound.

## One step preparation of supported catalysts

Numerous possibilities offered for the simultaneous synthesis, just by combining the precursors. From this variety of cases, several combinations have been tried, presenting potential interest for catalysis.

Phase composition of products issued from the simultaneous reactions of precursor salts in molten  $\text{NaNO}_3\text{-KNO}_3$  at 500 °C

Oxidation(s) oxide	$\text{SO}_4^{2-}$	$\text{MoO}_4^{2-}$	$\text{VO}_4^{2-}$	$\text{PO}_4^{3-}$
Al	$\text{Al}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{Al}_2\text{O}_3$
Zr	$\text{ZrO}_3$	$\text{ZrO}_3$	$\text{ZrO}_3$	$\text{Na}_4\text{Zr}(\text{PO}_4)_4$
Ti	$\text{TiO}_2$	$\text{TiO}_2$	$\text{TiO}_2$	$\text{Na}_4\text{Ti}(\text{PO}_4)_4$
Zn	$\text{ZnO}$	$\text{ZnO}$	$\text{Na}_2\text{ZnVO}_4$	$\text{Na}_2\text{ZnPO}_4$
Mg	$\text{MgO}$	$\text{MgMoO}_4$	$\text{Na}_4\text{Mg}(\text{VO}_4)_4$	$\text{Na}_4\text{Mg}(\text{PO}_4)_4$
Ni	$\text{NiO}$	$\text{NiMoO}_4$	$\text{NaNiVO}_4$	$\text{NaNiPO}_4$
Ca	$\text{CaSO}_4$	$\text{CaMoO}_4$	$\text{NaCa}_4(\text{VO}_4)_3$	$\text{NaCaPO}_4$

## Preparation and characterization of lanthanum nickel oxides by combined coprecipitation and molten salt reactions

- Coprecipitation combined with high temperature melting was used to form lanthanum nickel oxides.
- The advantage of this method is that salts, such as NaCl, LiCl or KCl that are formed as by products during co-precipitation were not washed out.
- They act as a flux in which the precipitates dissolve and react to give oxides

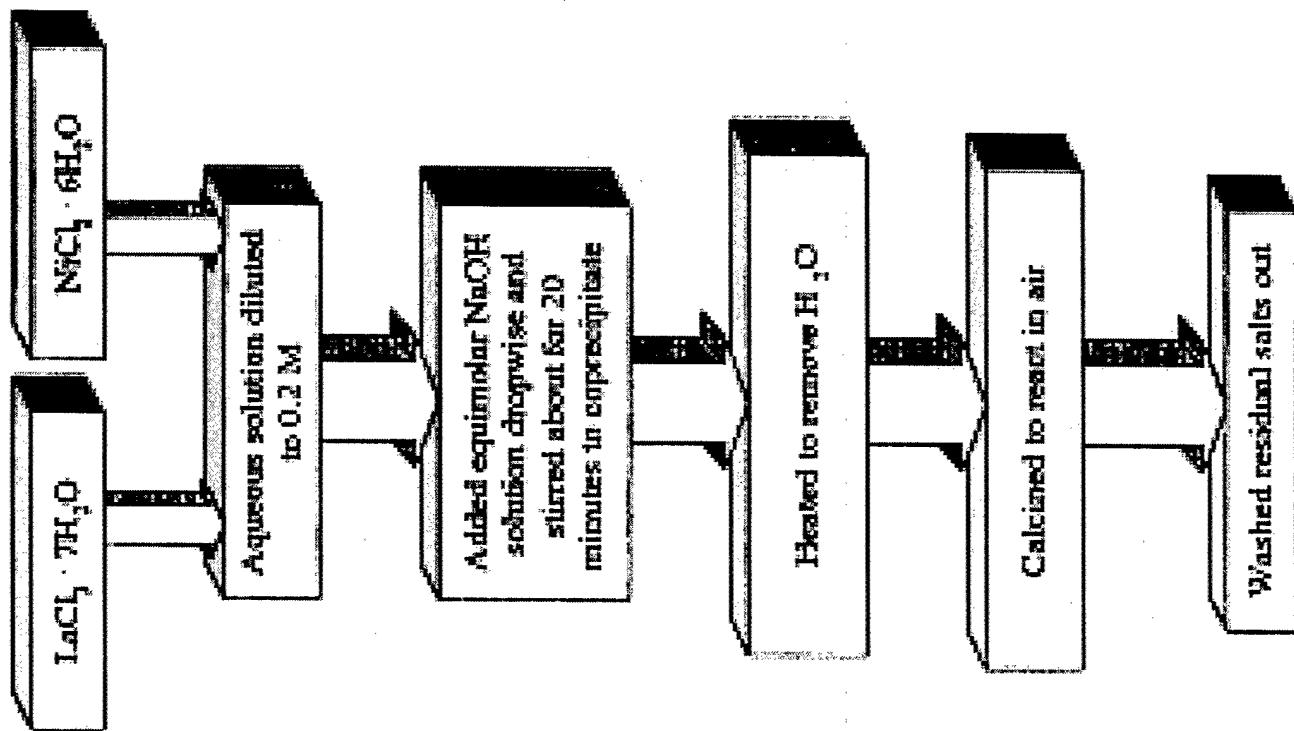
(a) La:Ni=1:1

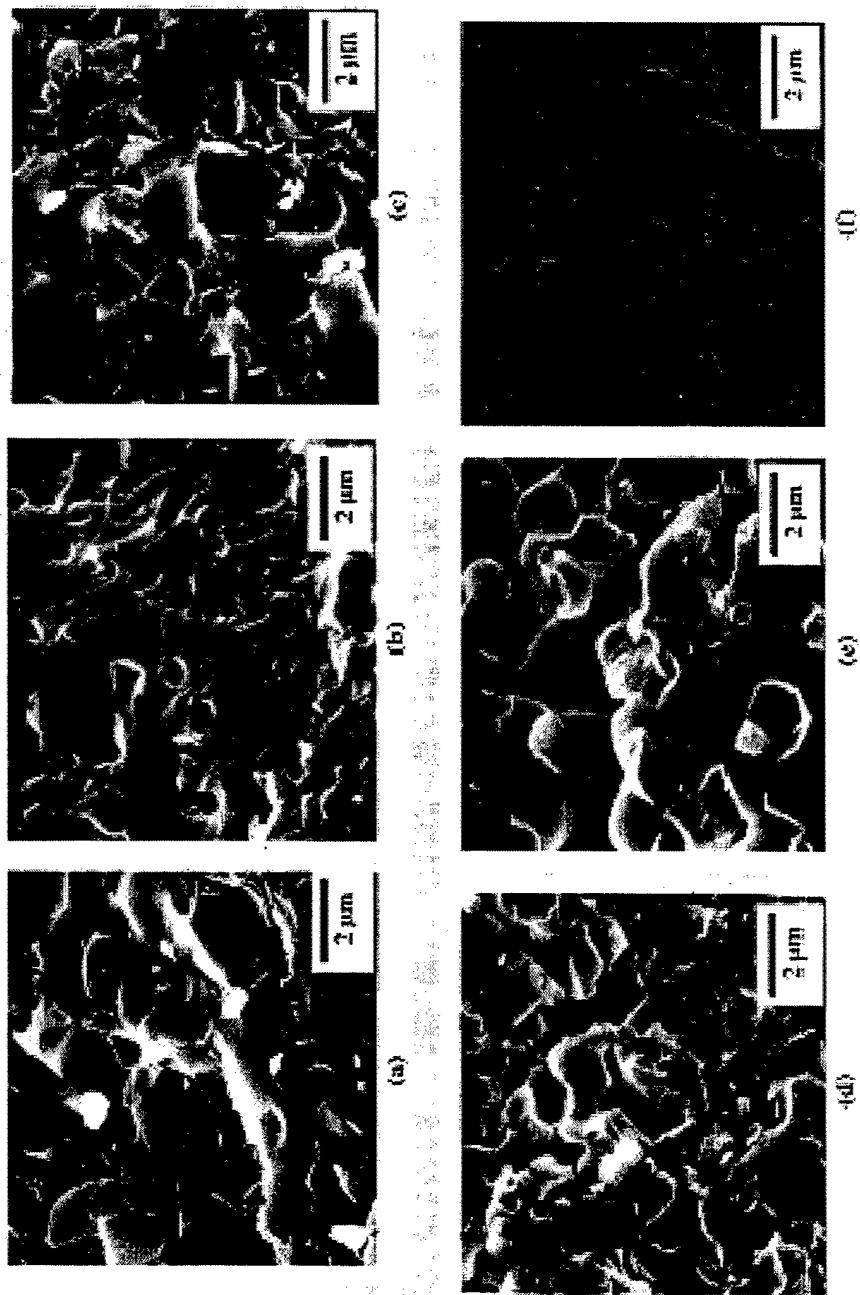


(b) La:Ni=2:1



SEM images in 5 K magnification of the coprecipitated samples in NaOH.





SEM images in 15 K magnification of the sintering samples: (a) La:Ni=1:1 at 1673 K with NaCl; (b) La:Ni=2:1 at 1573 K with NaCl; (c) La:Ni=1:1 at 1673 K with KCl; (d) La:Ni=2:1 at 1573 K with KCl; (e) La:Ni=1:1 at 1673 K with LiCl; (f) La:Ni=2:1 at 1573 K with LiCl.

1. The  $\text{LaNiO}_3$  and  $\text{La}_2\text{NiO}_4$  could be obtained from coprecipitating with  $\text{NaOH}$  or  $\text{KOH}$  in about 0.2-0.4 M aqueous solution, but not with  $\text{LiOH}$
2. According to the experimental results, the  $\text{LaNiO}_3$  and  $\text{La}_2\text{NiO}_4$  could be synthesized by calcining its precursor at 1073 K for 8 h with  $\text{NaCl}$  and at 1173 K for 8 h with  $\text{KCl}$ , respectively.
3. Using  $\text{NaCl}$  as a flux, the formation of  $\text{LaNiO}_3$  is best at 1073 K and some is converted to  $\text{La}_2\text{NiO}_4$  at 1173 K.
4. The reaction temperature is lower for  $\text{LiCl}$  as auxiliary melting.

*(In the course of this study a clear crystalline phase  $\text{Li}_2\text{NiO}_2$  was discovered at 973 K).*

## Synthesis of superconducting $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ by a modified molten salt process

A modified molten salt process has been developed to directly synthesise the superconducting  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ . Advantages over other known synthetic procedures in which either multiple steps are necessary (ceramic method) or the chemical composition and the superconducting properties may depend on various factors (electrolytic method):

- low temperature synthesis,
- single-step reaction
- easy control of stoichiometry.

*Further, this process may, potentially, be extended to other related systems.*

By using KOH as flux, a low temperature synthetic method has been used to prepare the K-doped BaBiO<sub>3</sub> in the past years [a-c]. For example, small sized crystals of Ba0.87K0.13BiO<sub>3</sub> [a] or a powdered form of Ba<sub>1-x</sub>K<sub>x</sub>BiO<sub>3</sub> consisting of at least two phases [b] have been obtained from the molten KOH-Ba(HO)<sub>2</sub>-Bi<sub>2</sub>O<sub>3</sub> system in air. By adding strong oxidizing agents, such as LiNO<sub>3</sub>, LiClO<sub>4</sub>, superconducting Ba<sub>0.6</sub>K<sub>0.4</sub>BiO<sub>3</sub> could also be prepared in a similar way [c]. However, the existing processes required either relatively high temperature (e.g.360°C) or prolonged synthetic time, since the oxidation of the active elements by air or other oxidizing agents in the presence of strong base is not expected to be high.

[a] J.P. Wignacourt, J.S. Swinnea, H. Steinink, J.B. Goodenough, *Appl. Phys. Lett.* 53 (1988) 1753.

[b] N.L. Jones, J.B. Parise, R.B. Flippen, A.W. Sleight, *J. Solid State Chemistry* 78 (1989) 319.

[c] L.Z. Zhao, B. Yin, J.B. Zhang, J.W. Li, C.Y. Xu, M. Xie, S.H. Liu, *Physica C* 723 (1997) 282-287.

✓ 20–30g in the form of pellets KOH into a Teflon crucible and melted at t= 200 - 260°C.

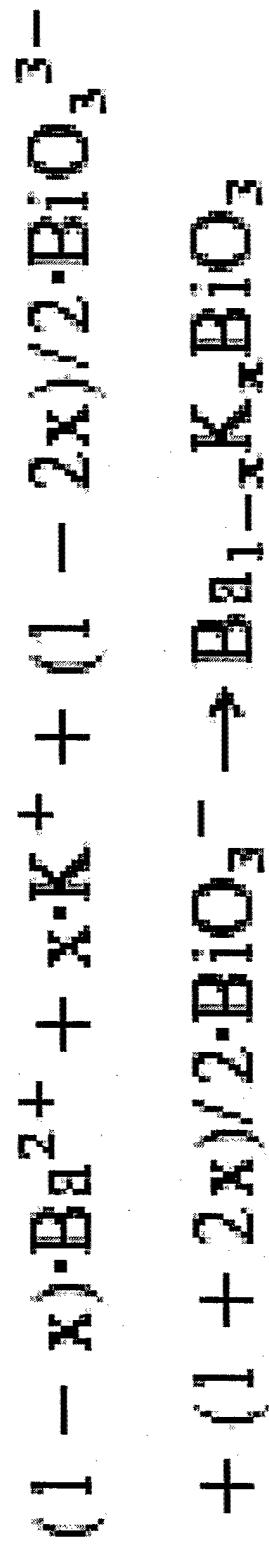
✓ After 30 min., a pre-ground mixture of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{NaBiO}_3$  and  $\text{Bi}_2\text{O}_3$  slowly added ( continuously stirring with a Pt bar), with mole ratio  $\text{NaBiO}_3$ :  $\text{Bi}_2\text{O}_3 = 2(11x)/(1-x)$  (i.e. ratio  $\text{Bi}^{5+}:\text{Bi}^{3+}$  ions in  $\text{Ba}_{1.2x}\text{K}_x\text{BiO}_3$ ), but with  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  slightly in excess vs. stoichiometry

✓ As soon as the mixture was added into melted KOH, a black precipitate was formed immediately. The melt was maintained for several hours at the above-mentioned temperatures to improve the homogeneity of the samples.

✓ Finally the liquid in the crucible was poured out, while the precipitate was kept and cooled to room temperature.

✓ The precipitates were thoroughly washed with distilled water to remove the residual KOH and, then, rinsed with ethanol and dried in air for a few hours at about 75°C.

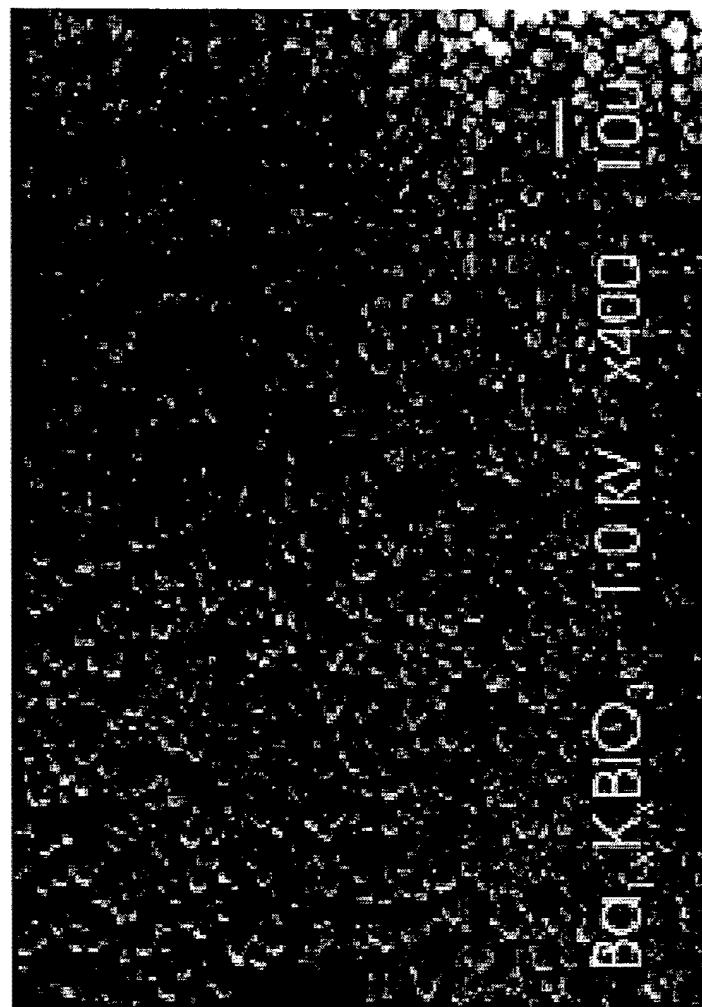
✓ The final products were fine powders.



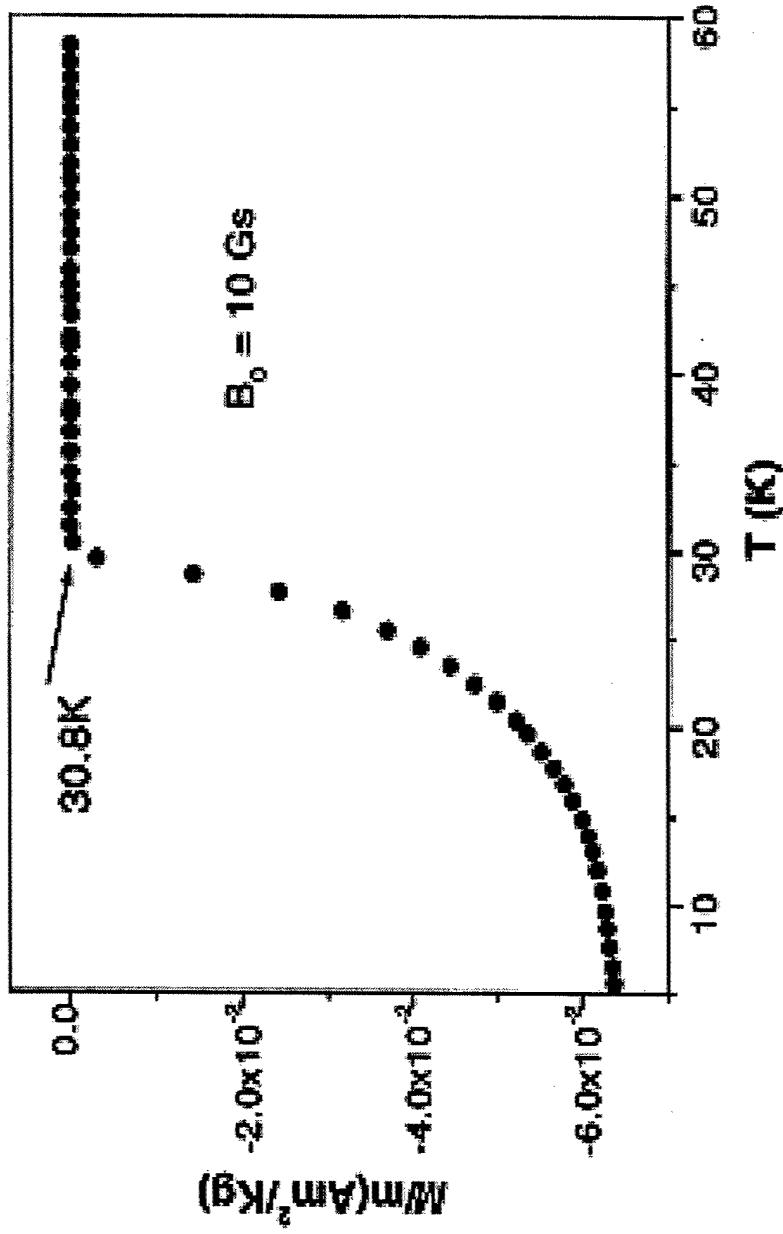
The actual reaction might be more complicated or involves chemical equilibrium since the oxidation (or reduction) of bismuth in air cannot be avoided and the KOH is much more abundant. This can be seen from the fact that using the stoichiometrically calculated amount of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{NaBiO}_3$  results in a composition of slightly higher K content.

## SEM of the $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ powders :

The particle sizes are of a few micrometers, and are quite uniform.

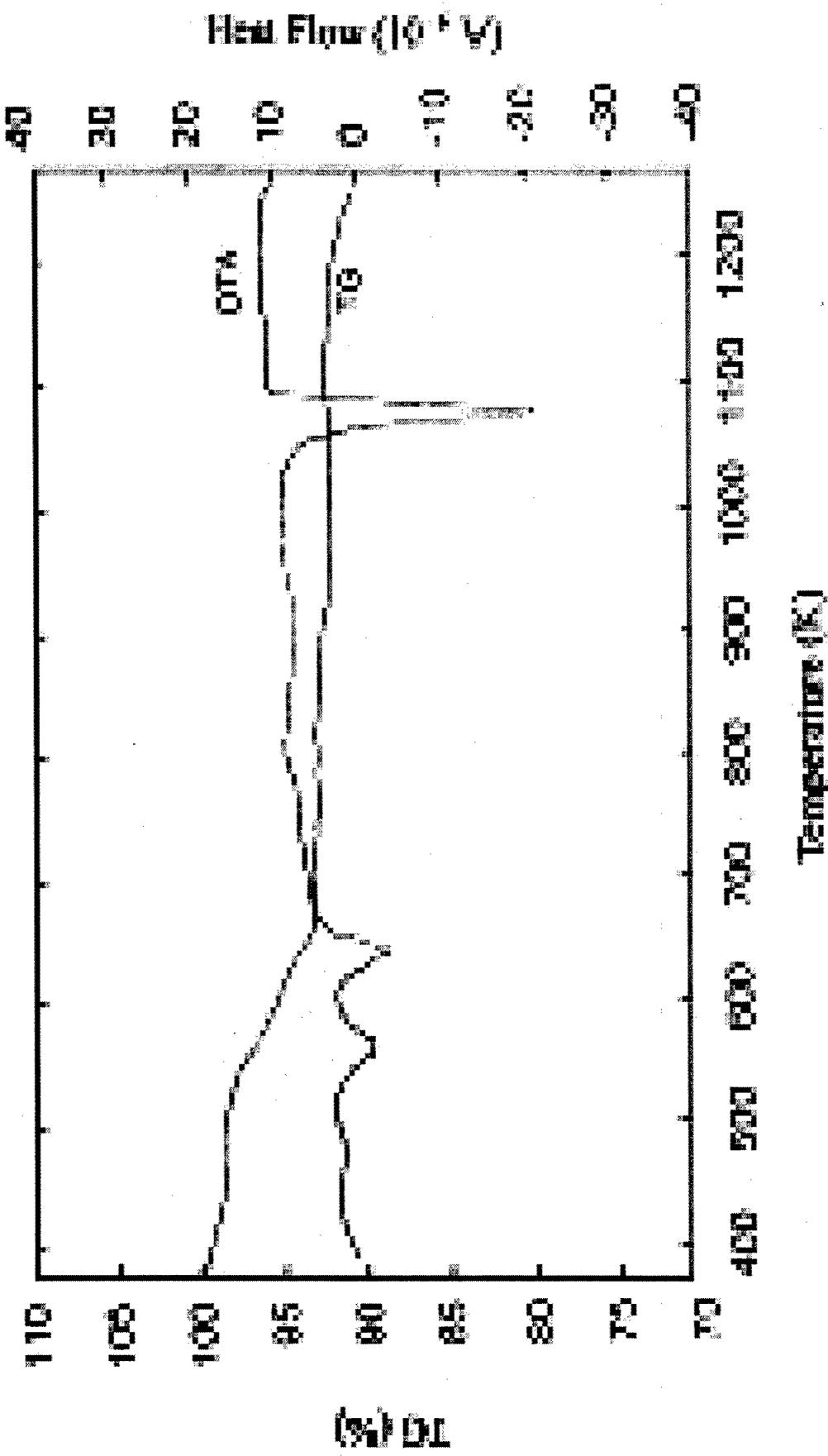


## AC susceptibility data of $\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$ .



The superconducting  $T_{\text{tr}}$  is about 30.8 K (i.e slightly  $>$  than the reported  $T_{\text{tr}}$  of ceramicically prepared  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  powders).

The transition is apparently very sharp, indicating a good homogeneity of the sample.



Thermogravimetric analysis and differential thermal analysis of the precursor.

## Fabrication of CoO nanorods via thermal decomposition of $\text{CoC}_2\text{O}_4$ precursor

- CoO nanorods with diameters of 10–80 nm and lengths of several micrometers have been successfully prepared by a simple and novel method.
- These CoO nanorods are structurally uniform, single crystalline.
- The growth mechanism of the CoO nanorods is similar to the molten salt synthesis.
- Particularly, surfactant NP-9/5 and NaCl flux are of critically importance for the formation of CoO nanorods.

**Nanorods** : great potential to provide an opportunity to test fundamental quantum mechanics concepts and to play a vital role in various applications such as photonics , nanoelectronics and data storage.

**Cobalt oxide CoO**: cubic rock-salt structure ; technologically important applications based on its magnetic or catalytic properties .

Synthesis of cobalt oxides nanocrystals up to now, many routes such as sol-gel , spray pyrolysis , chemical vapor deposition , chemical precursor routes, electro-chemical and sonochemical synthesis

.....

**fabrication of CoO nanorods**: a simple and novel method by calcining the precursor of  $\text{CoC}_2\text{O}_4$  obtained via chemical reaction between  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  and  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  in the presence of NP-9/5 and NaCl flux.

Starting materials: cobalt acetate  $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ , oxalic acid  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ , nonyl phenyl ether (9)/(5)(NP-9/5) and NaCl.

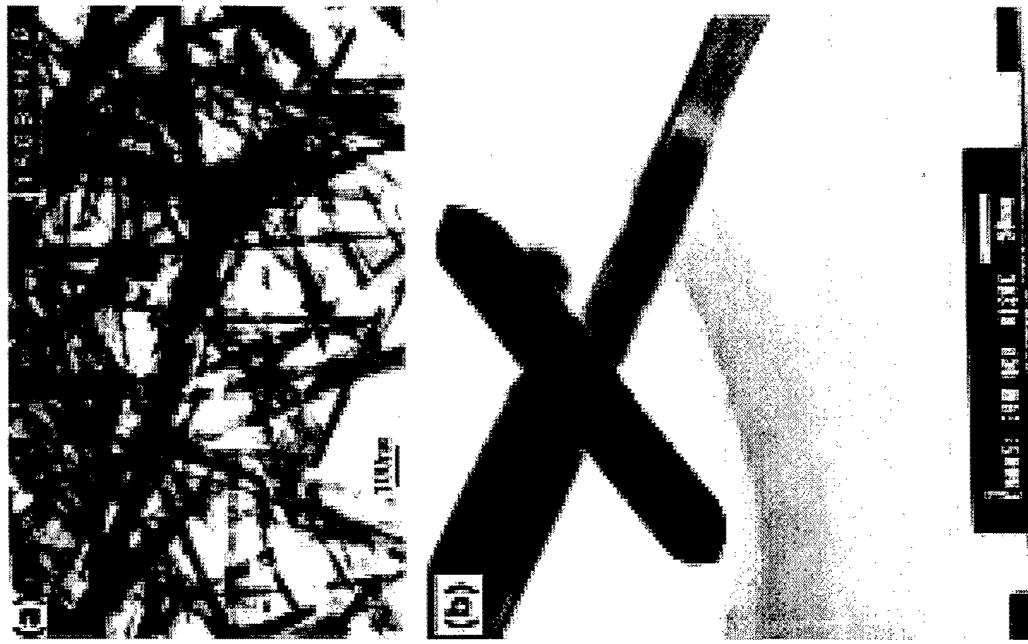
- $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  (4.98 g) and  $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  (2.53 g) according to 1:1 molar rate were mixed with 5 ml of NP9/5 in a mortar, ground for several minutes and kept in a thermostat oven at 50–60 °C for 6 h to prepare the precursor, the product was washed several times with distilled water and acetone to remove remaining reactants, NP9/5 and by-product,
- and then dried in an oven at 70–80 °C for 12 h.
- The obtained product was collected for the fabrication of CoO nanorods.  $\text{CoC}_2\text{O}_4$  (2 g) was simultaneously mixed with 8 g of NaCl powder and then ground for several minutes. The ground mixture was annealed at 900 °C for 2 h. Following heat treatment, it was gradually cooled to room temperature (5 °C/min), the as-prepared product was washed with distilled water, ethanol and then ethyl ether by an ultrasonic bath and a centrifuge.

General TEM morphologies  
of

the synthesized product.  
mostly composed of solid  
rod-like structures.

(a), smooth nanorods, 10-80  
nm diameter, length ranging  
1- 3 um.

(b) typical nanorod with  
conical tips at both ends,  
about 50 nm.



## Preparation of lanthanum nickel strontium oxides

- $\text{LaNiO}_3$  has attracted much attention in the past few years, because of technologically important applications (conducting layer for application in ferroelectric memories, electrode for high temperature fuel cells , catalyst and as a sensor for ethanol.
- $\text{LaNiO}_3$  is a cubic or rhombohedrally distorted perovskite-type structure. Its thermal stability is not so high (1170K) because of a partial reduction of  $\text{Ni}^{3+}$  to  $\text{Ni}^{2+}$  induced by oxygen partial pressure during heating. Therefore,  $\text{LaNiO}_3$  is converted to  $\text{La}_2\text{NiO}_4$ , as a two-dimensional structure of  $\text{K}_2\text{NiF}_4$
- The substitution of  $\text{La}_{3+}$  in  $\text{LaNiO}_3$  by  $\text{Sr}_{2+}$  would reduce the  $\text{Ni}_{3+}$  change to  $\text{Ni}_{2+}$  for assuring the cubic perovskite structure .

*Chen-Feng Kao, Chiang-Lih Jeng - Ceramics International 26 (2000) 237-243*

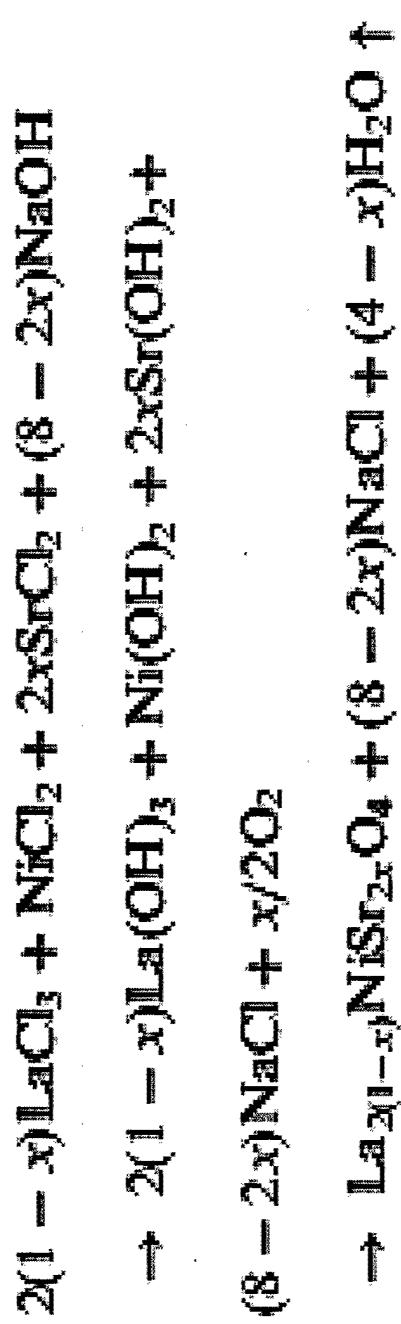
## Method: combined coprecipitation and molten salt reactions

1.  $\text{La}_{1-x}\text{NiSr}_x\text{O}_3$  and  $\text{La}_{2(1-x)}\text{NiSr}_2\text{xO}_4$  obtained from coprecipitating with  $\text{NaOH}$  in about  $0.2\text{-}0.4\text{ M}$  of corresponding metal chlorides in ethyl alcohol solution ; particle size :  $0.1\text{ mm}$ .
2. limiting amount of  $\text{Sr}^{2+}$  dopant for  $\text{La}_{1-x}\text{NiSr}_x\text{O}_3$  and  $\text{La}_{2(1-x)}\text{NiSr}_2\text{xO}_4$  :  $x=0.15$  and  $0.30$ , respectively. Further doping with  $\text{Sr}^{2+}$  would induce appearance of other compounds, such as  $\text{La}_{1.5}\text{NiSr}_{0.5}\text{O}_4$ .
3.  $\text{LaNiO}_3$  , doped with  $\text{Sr}^{2+}$  , would maintain its perovskite phase at higher temperature (no reduction of  $\text{Ni}^{3+}$  convert to  $\text{Ni}^{2+}$ ).

This process control is much easier

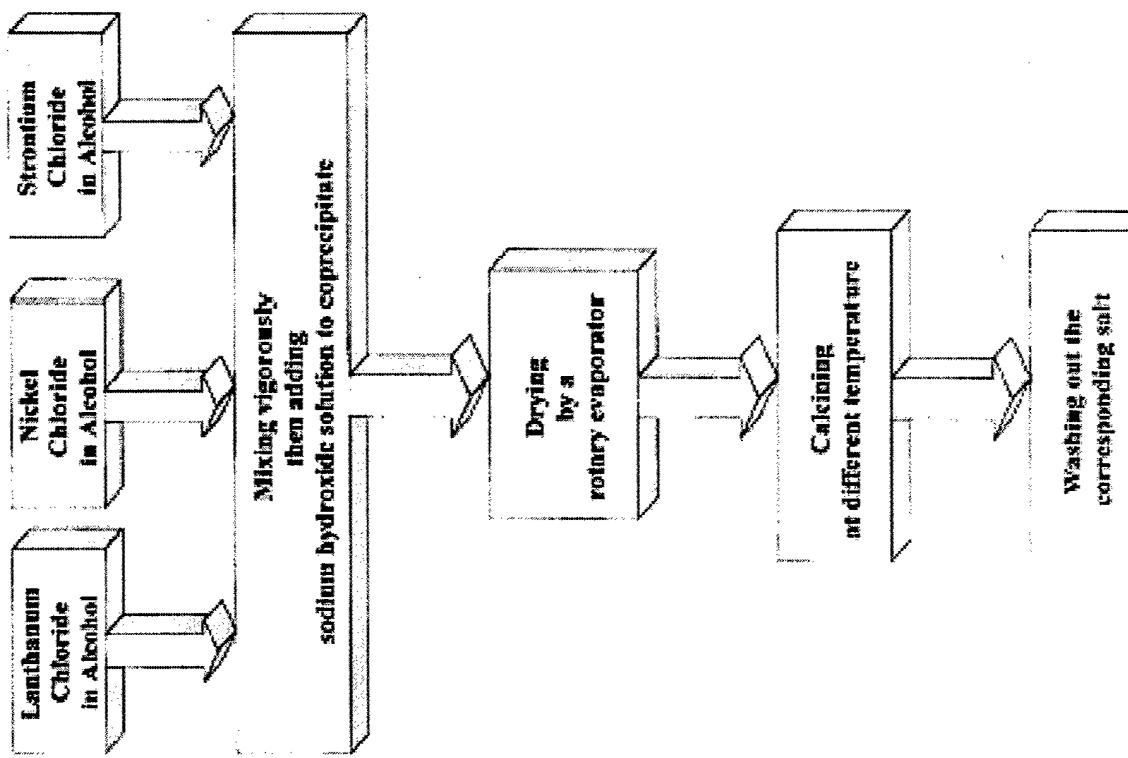
The oxides have more uniform and much better particle size distribution than that of solid-state reaction or general chemical coprecipitation (*the general chemical coprecipitation process needs to wash the precursors with distilled water and to filtrate repeatedly that would make serious deviations from stoichiometry*).

The reactions can be written as follows:



- Chloride mixture dissolved in absolute ethyl alcohol and diluted to 0.2 M.

- Saturated NaOH aqu. solution used to mix with the above solution to form a lanthanum nickel strontium hydroxide precursor.
- The rotary evaporator was used to obtain the dry precursors and to recover the alcohol for reuse.



The salt was acted as a flux to improve the reactivity of precursor.

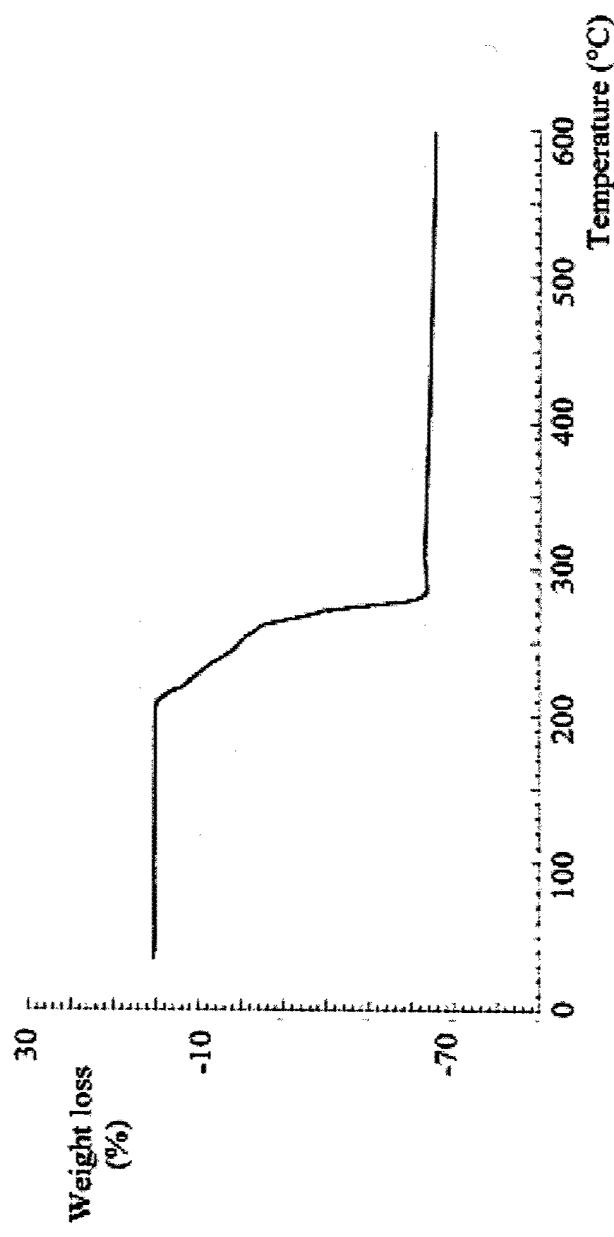
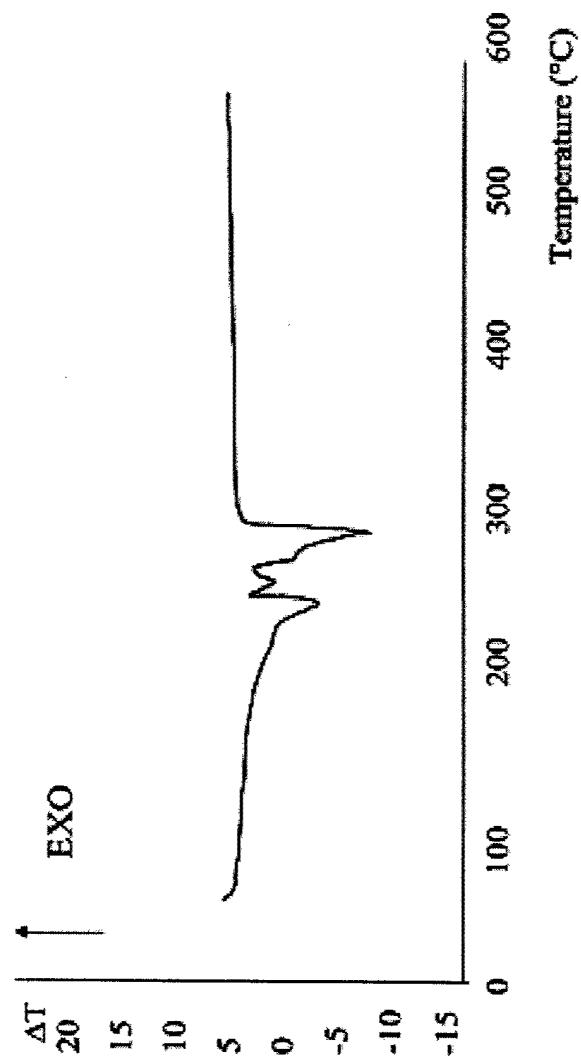
## NANOSIZED CeO<sub>2</sub> POWDERS OBTAINED BY FLUX METHOD

- Nanosized and well-crystallized Ce(IV) oxide powder was prepared by the flux method at relatively low temperature (600°C), utilizing cerium(IV) salt and different eutectic molten salt mixtures
- Very simple ; lead to powders with desirable characteristics, including very fine size, narrow size distribution, single-crystal particles, high purity, and good chemical homogeneity.
- Same advantages as the hydrothermal technique ( low cost, elimination of the calcination process) but does not require elevated temperature and pressure.

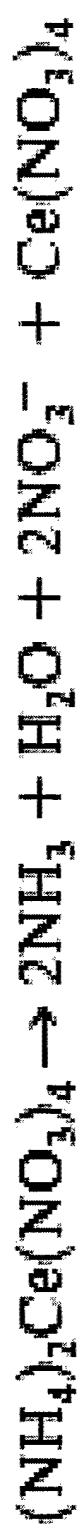
## Sample Preparation.

- ❑ molten salt reactions in alumina crucibles at 600°C.
- ❑ Solvents: KOH/NaOH, NaNO<sub>3</sub>/KNO<sub>3</sub>, and LiCl/KCl eutectic mixtures chosen, due to their low melting temperatures (170, 225, and 355°C, respectively)
- ❑ The Ce(IV) precursor cerium ammonium nitrate (NH<sub>4</sub>)<sub>2</sub>Ce(NO<sub>3</sub>)<sub>6</sub> was added in a 1:1 ratio to the molten salt at the reaction temperature.
- ❑ The melt was maintained at maximum temperature for 120 min. After being quenched to room temperature, the reaction products were separated from the soluble alkali salts by washing with distilled water and then were dried in air at 100°C.

DTA & TGA  
curves of  
 $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$

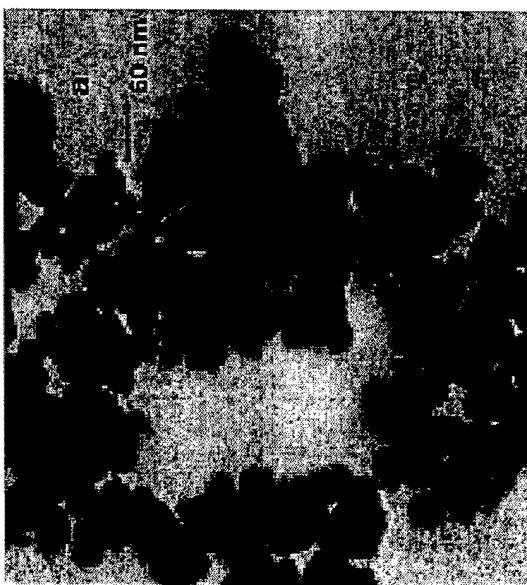


A four-endothermic-step transformation according to the following equations:

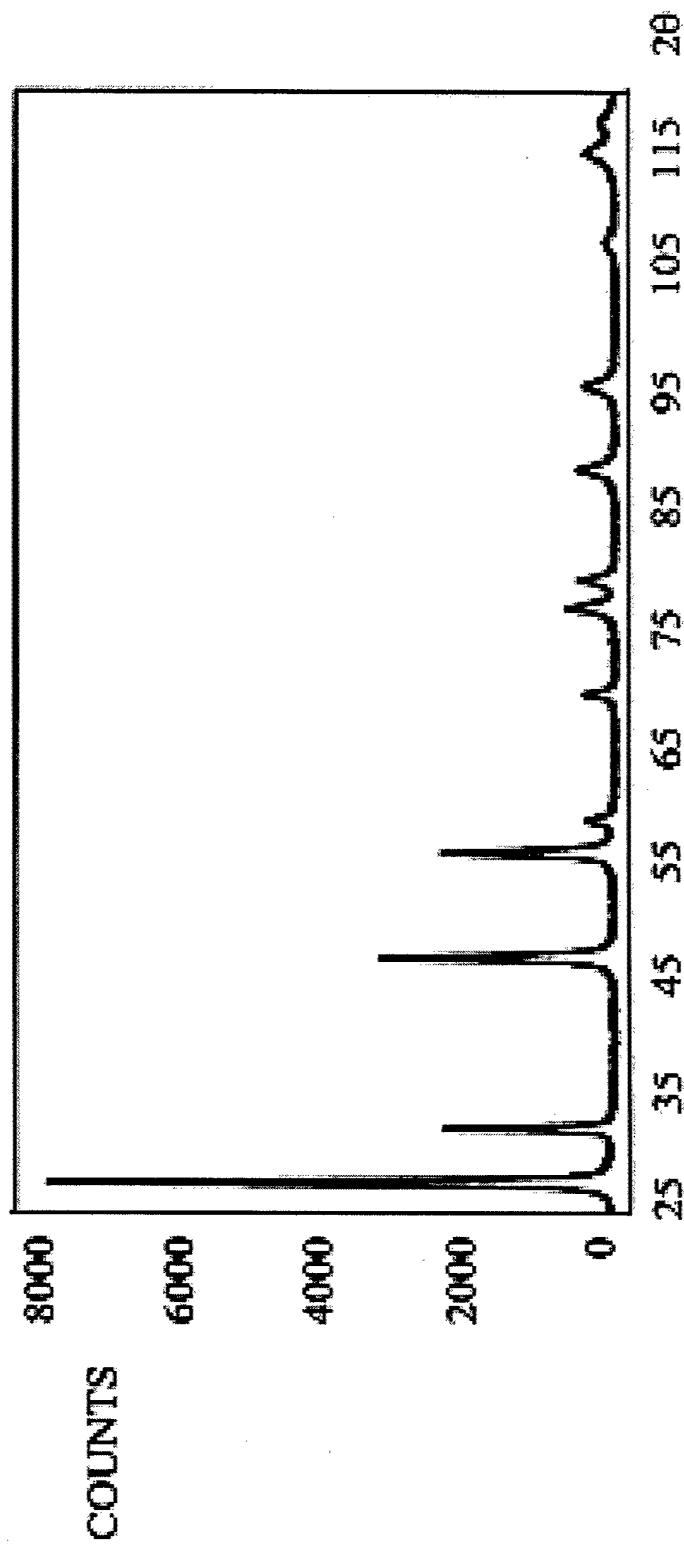


**TEM micrographs of the  
ceria powders obtained by  
fluxes of**

- (a) hydroxides,
- (b) nitrates, and
- (c) chlorides.



The XRD analysis of the as-prepared powders showed the same crystalline structure for all the fluxes used. Peaks were attributed to crystalline cerium oxide,  $\text{CeO}_2$ , with a cubic fluorite structure



### Average Powders Particle Size Calculated by Various Methods

Methods	Flux used		
	Hydroxides	Nitrates	Chlorides
XRD (nm)	18	25	16
TEM ( $\pm 3$ nm)	20	20.5	14
BET (nm)	23	28	20

## TEXTURED MICROSTRUCTURES IN BARIUM HEXAFERRITE

- **Seeded reactive matrix and templated grain growth used to produce highly textured materials in the barium hexaferrite system.**
- **This technique, in which seeds are obtained by molten salt synthesis (MSS), provides more flexibility for producing textured microstructures than tape casting or uniaxial pressing.**
- **Since the texture direction is coupled only to the direction of the applied magnetic field, a wide variety of sizes and shapes of textured components are afforded.**
- **It is anticipated that this technique can be employed for a variety of magnetically anisotropic materials.**

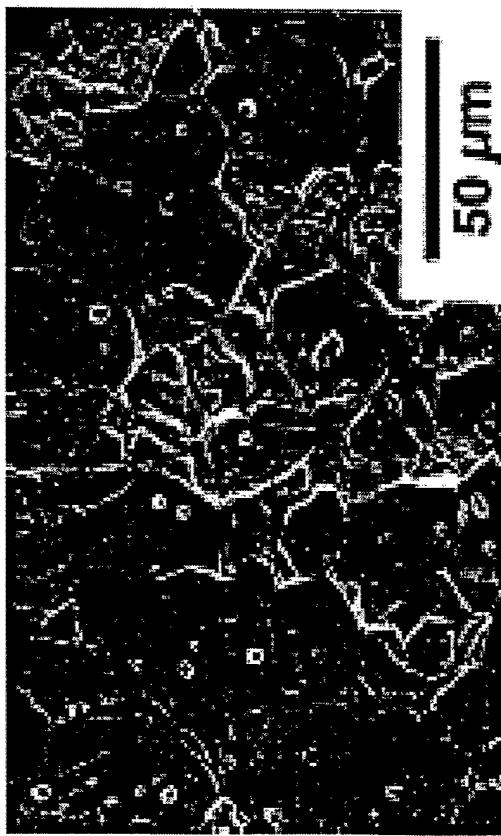
Two components are needed in order to make textured barium hexaferrite by combined magnetic field assisted gelcasting and TGG techniques.

- First, a non-magnetic precursor to barium hexaferrite must be developed that can meet the suspension requirements of gelcasting (starting materials)  $Fe_2O_3$ : $BaCO_3$ : (molar ratio 5:6:1) with 1.5% by mole of B2O3 and (gel) HMA M initiated with approximately 0.5mL/g slurry of APS TMED) The solids loading was 40% by volume. Surfynol CT-131 (was used as the surfactant. The slurries were ball milled
- Second, seed particles must be produced that are sufficiently anisotropic to serve as templates for texturing.

At high temperatures, the iron oxide and barium carbonate react to form a fine-grained barium ferrite matrix surrounding the previously aligned barium ferrite seeds.

Anisotropic “seed” particles were produced using a two-stage molten salt synthesis (MSS).

- First,  $\text{Fe}_2\text{O}_3$  and  $\text{BaCO}_3$  were mixed with  $\text{KCl}$  as the fluxing agent at a 1:1 reactants:salt weight ratio. Heating to  $900^\circ\text{C}$  for hours in an  $\text{Al}_2\text{O}_3$  crucible produced plate-shaped  $\text{BaFe}_{12}\text{O}_{19}$  particles approximately 1 mm in diameter.
- To coarsen the particles, the  $\text{BaFe}_{12}\text{O}_{19}$  plates from the  $\text{KCl}$  melt were mixed with  $\text{BaCl}_2$  and  $\text{Fe}_2\text{O}_3$ . The  $\text{BaCl}_2:\text{Fe}_2\text{O}_3$  ratio was 2:1 by weight and the  $\text{Fe}_2\text{O}_3:\text{BaFe}_{12}\text{O}_{19}$  ratio was 500:1 by mole. Heating to  $1150^\circ\text{C}$  for 8 hours produced particles ranging from 5–25 mm and approximately 1–2 mm thick. These were deemed adequate for templated grain growth and are shown in Figure 1.



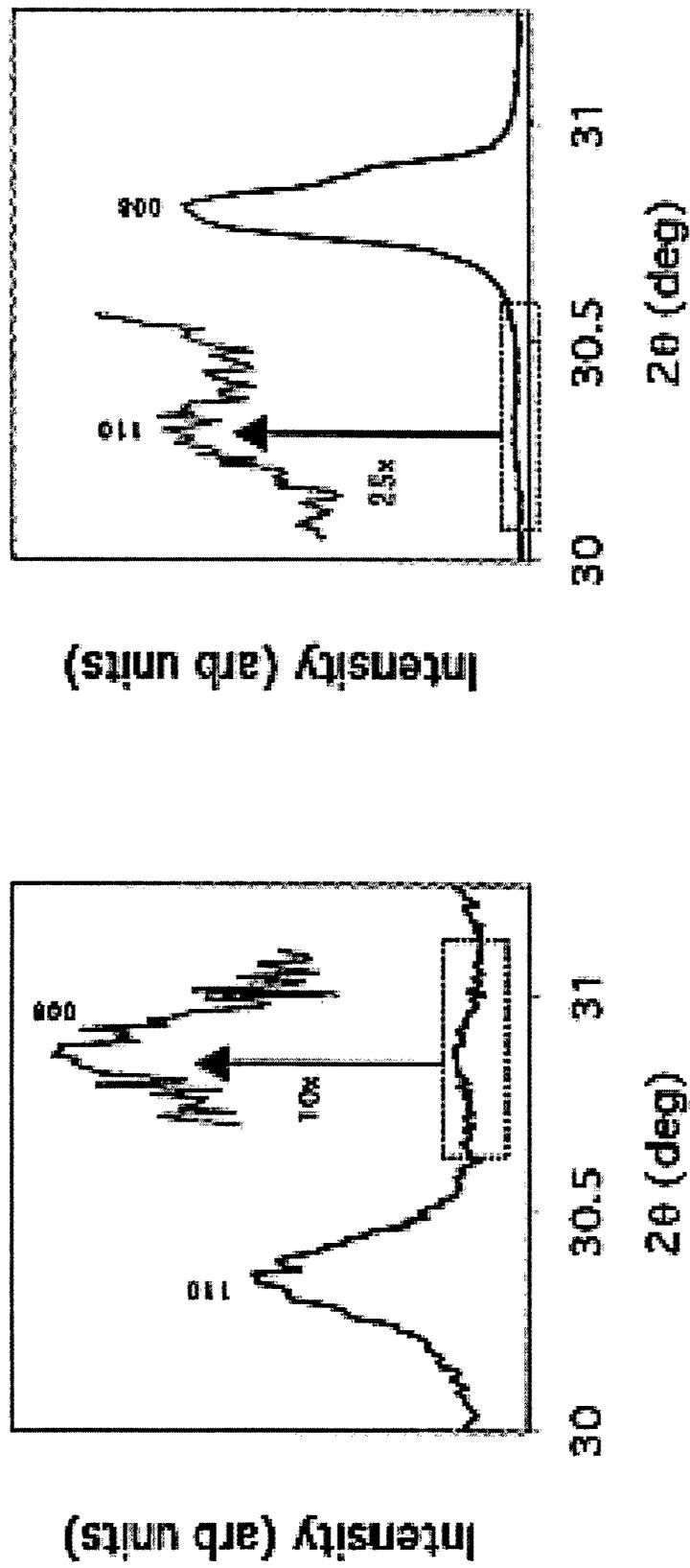
(a)



(b)

SEM micrographs of the control (a) and magnetically-aligned (b) samples.

The control samples possess a large grain size (20–30mm), but not the plate-like shape indicative of textured barium hexaferrite. The magnetically-aligned samples possess a large grain size (25–50mm), plate-like shape, and a definitive preferred orientation.



Relative intensities of the (110) and (008) peaks in the control and magnetically aligned samples (Note difference in amplification of smaller peak).

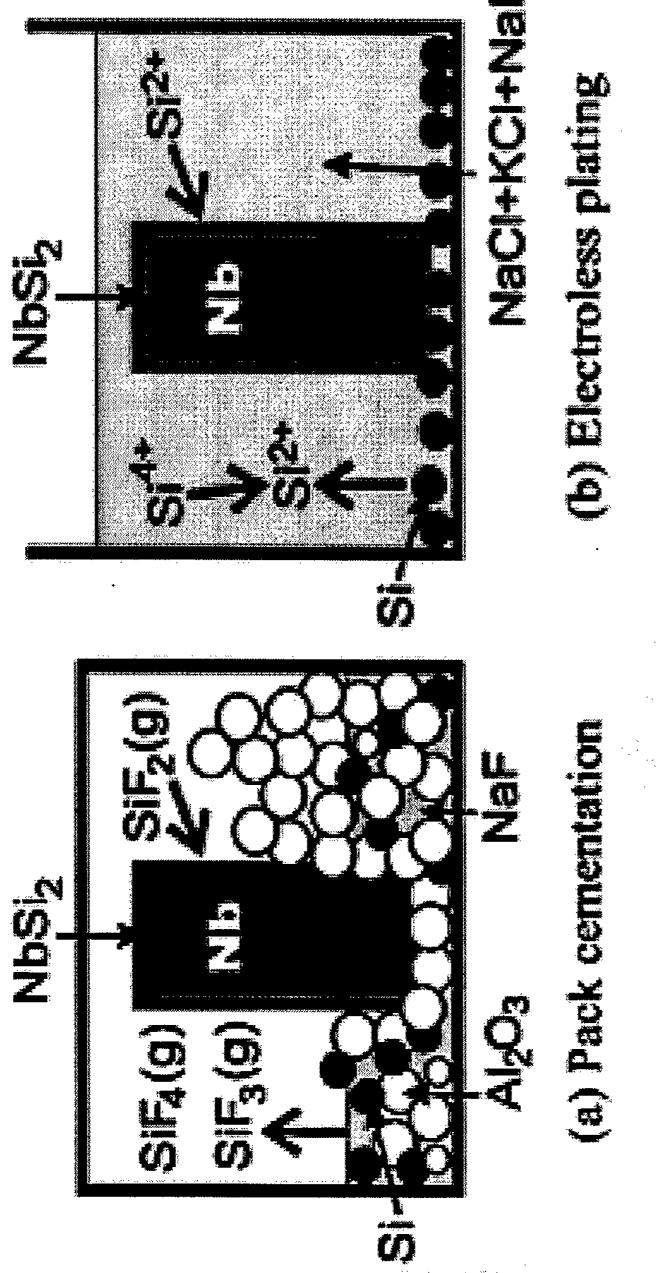


Molten salt synthesized "seed" particles of barium hexaferrite.

- The flux method is a well-known method used for single-crystal growth , but it has seldom been applied to the synthesis of nanocrystalline particles.
- This method is very simple and can lead to powders with desirable characteristics, including very fine size, narrow size distribution, single-crystal particles, high purity, and good chemical homogeneity. As with the hydrothermal technique, the main advantages of this method are not only low cost, but also the elimination of the calcination process.
- In addition, the flux method does not involve the elevated temperature and pressure (4 h at 300°C, 10 MPa) characteristic of the hydrothermal technique.

## NbSi coating on niobium using molten salt

- For obtaining better oxidation resistance of niobium in air, a niobium silicide was non-electrolytically deposited onto Nb from a molten salt, where a disproportional reaction occurs between  $\text{Na}_2\text{SiF}_6$ ,  $\text{SiO}_2$ , and Si. A single phase of  $\text{NbSi}_2$  was formed with a homogeneous thickness of about 10 nm above 1073 K.
- The oxidation resistance of pure niobium with this coating layer was improved.
- During the oxidation at the high temperatures,  $\text{Nb}_5\text{Si}_3$  was formed at the interface between the Nb substrate and the  $\text{NbSi}_2$  layer. Due to this intermediate layer formation, the oxidation resistance became better than for pure  $\text{NbSi}_2$



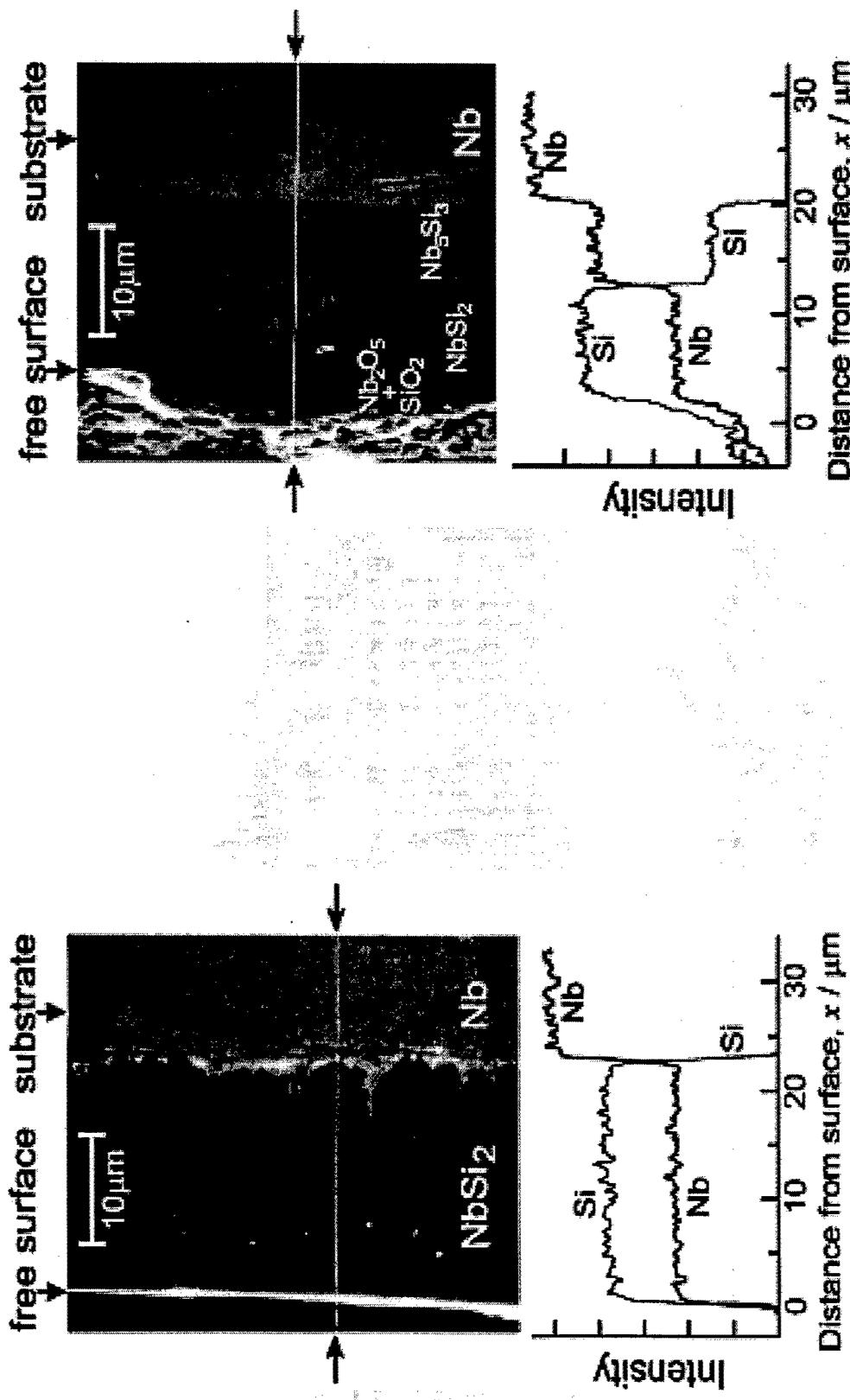
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- (a) Pack-cementation method : low cost, good adhesion coating but requires encapsulation and a high vapor pressure at temperatures as high as 1273–1473 K.
- (b) Electroless plating: operable in open air at 973–1173 K

When  $\text{Na}_2\text{SiF}_6$  and Si powder are added in the supporting salt of  $\text{NaCl}-\text{KCl}$ , a disproportional reaction between Si and  $\text{Si}^{4+}$  ions deposits a siliconized layer on the metallic substrates, M, as,



The deposited Si from  $\text{Si}^{2+}$  penetrates into the metal surface, and forms an alloy (M-Si) with the metal substrate. The total reaction,  $\text{Si (particle in the molten salt)} + \text{M(substrate)} \Rightarrow \text{M-Si (siliconized layer)}$ , shows that the reaction is driven by the difference between the thermodynamic activity of pure silicon and that of the siliconized layer.



SEM image of the cross-section for the Nb sample siliconized at 1173 K for 7.2 ks. Nb and Si concentration were analyzed along the white line in the SEM image.

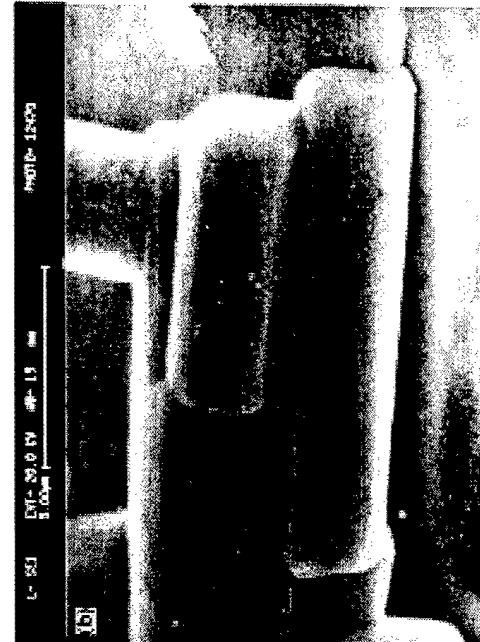
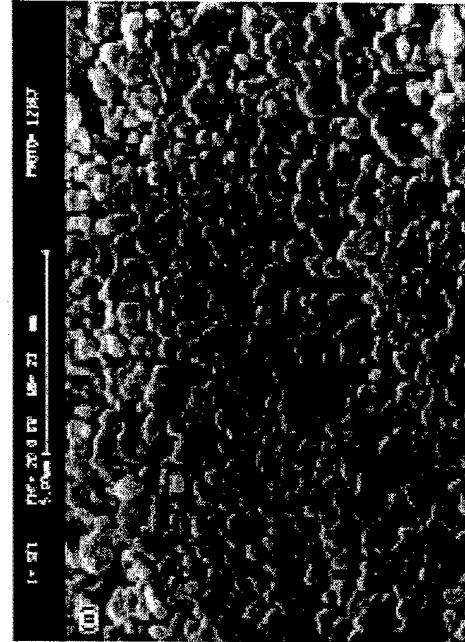
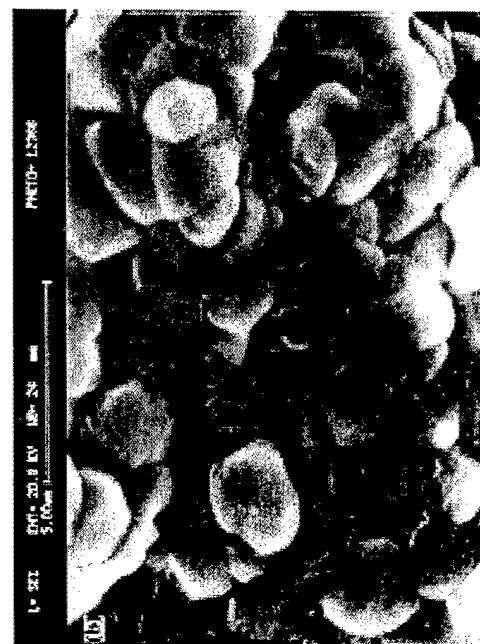
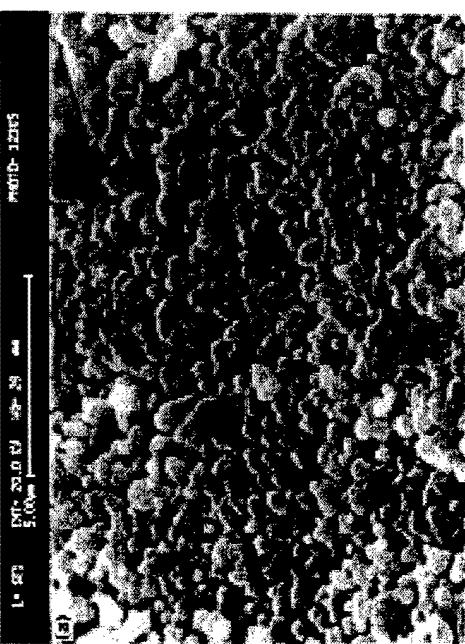
SEM image of the cross-section for the Nb sample siliconized at 1173 K for 7.2 ks. The sample was heated up to 1523 K in air. Nb and Si concentration were analyzed along the white line in SEM image.

A wide range of ceramic powders, including both single and complex perovskite ceramic system, have been synthesized in various molten salts.

- Alumina and zirconia powders by decomposing aluminum sulfate or aluminum chloride and zirconium sulfate in molten nitrates or nitrates salts, respectively.
- Binary oxides of perovskite structure, such as  $\text{BaTiO}_3$ - $\text{SrTiO}_3$  and  $\text{BaZrO}_3$ - $\text{SrZrO}_3$  : in the  $\text{NaOH}$ - $\text{KOH}$  molten salt eutectic @573 K.
- Lead niobate : in molten  $\text{KCl}$ - $\text{NaCl}$
- $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PFN) in  $\text{NaCl}$  and  $\text{KCl}$  @ 800°C,
- lead magnesium niobate** in  $\text{KCl}$  and  $(\text{Li},\text{Na})\text{SO}_4$  Both the reaction temperature and excess lead in the starting composition were shown to strongly affect the amount of perovskite phase formed in the molten salts.
- $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  : in  $\text{KCl}$  flux

## Molten salt synthesis of complex perovskite-related dielectric oxides

- Several important dielectric materials ( $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ,  $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  and  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ ), crystallizing in the cubic perovskite structure, at low T (900°C) with short time of heating using  $\text{NaCl}-\text{KCl}$  mixtures as flux.
- Sintering at 1000°C retains the disordered cubic structure.
- After the 1300°C sintering there is a slight decomposition to  $\text{Ba}_5\text{Nb}_4\text{O}_{15}$  in the niobates and nearly complete decomposition to  $\text{Ba}_{0.5}\text{TaO}_3$  in the case of  $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ .
- The reactivity of the oxide is much higher due to the initial flux treatment. Large faceted grains of size 7–10 microns, were observed in these samples after sintering at 1300°C. The grain size appears to depend on the initial time period of treatment with the flux.



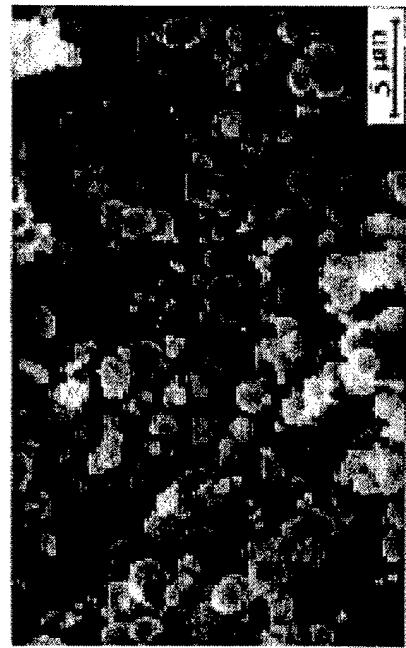
SEM of  $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (a) sintered at  $1000^\circ\text{C}$  (b) sintered at  $1300^\circ\text{C}$  (initial flux treatment  $900^\circ\text{C}/3$  h).

SEM of  $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (a) sintered at  $1000^\circ\text{C}$  (b) sintered at  $1300^\circ\text{C}$  (initial flux treatment  $900^\circ\text{C}/6$  h).

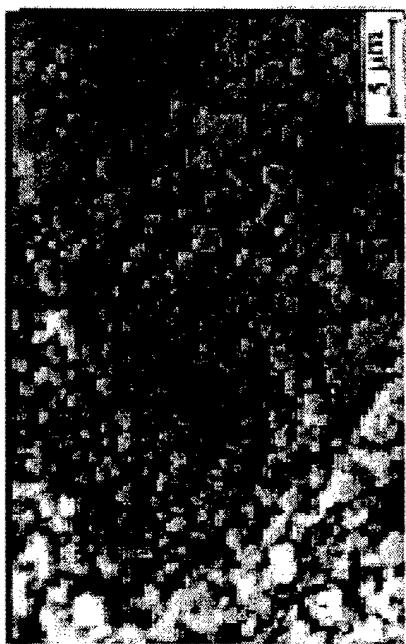
## Formation of lead magnesium niobate synthesized from molten potassium chlorate

- Lead magnesium niobate powders were prepared by reacting PbO, MgO and NbO in molten potassium chlorate. The formation of a single phase perovskite PMN requires a combination of 100 mol % excess lead oxide and a reaction temperature of 900°C.
- The choice of potassium chlorate as a flux is on the consideration that it is a powerful oxidizing agent, which may be useful in forming the perovskite phase of PMN. As reported, an oxidizing atmosphere is beneficial to prevent the formation of pyrochlore phase in the conventional solid state reactions

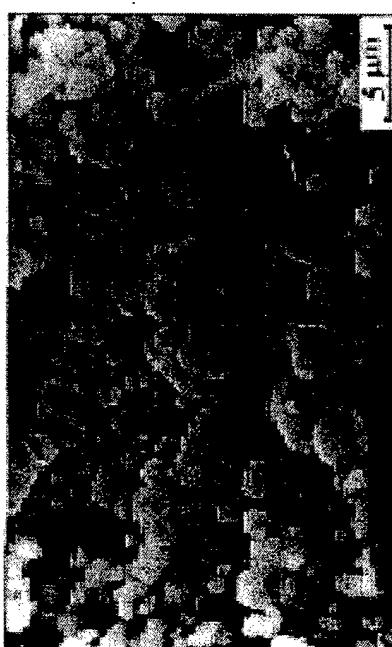
- The average particle size of resulting PMN powders increases with increasing reaction temperature and the amount of excess lead oxide added, while the particles undergo a change from a round to a cubical morphology. Too much excess PbO (.100 mol %) in the starting composition promoted grain growth in the molten salt-derived PMN ceramics, although the sintered density is not much affected at 1200°C and above. It also degrades the dielectric properties of sintered PMN, as a result of the occurrence of PbO-rich precipitates at the grain boundaries and grain junctions.



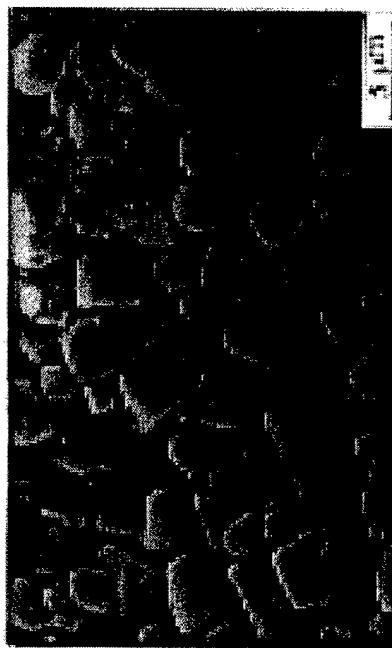
(A)



(B)



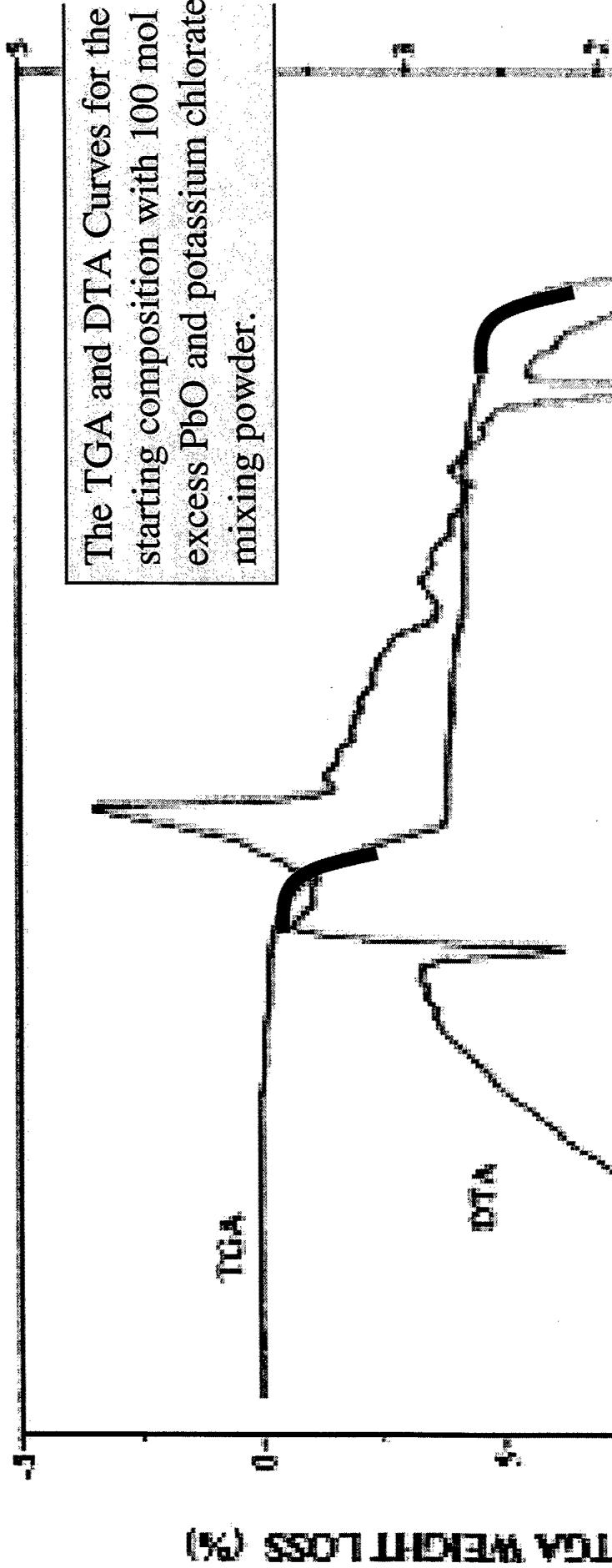
(C)



(D)

SEM Micrographs of the PMN powders formed in the compositions containing 0, 50, 100 and 200 mol % excess lead oxide, respectively, at 900°C for 2 h.

The TGA and DTA Curves for the starting composition with 100 mol % excess PbO and potassium chlorate mixing powder.



TGA curve :

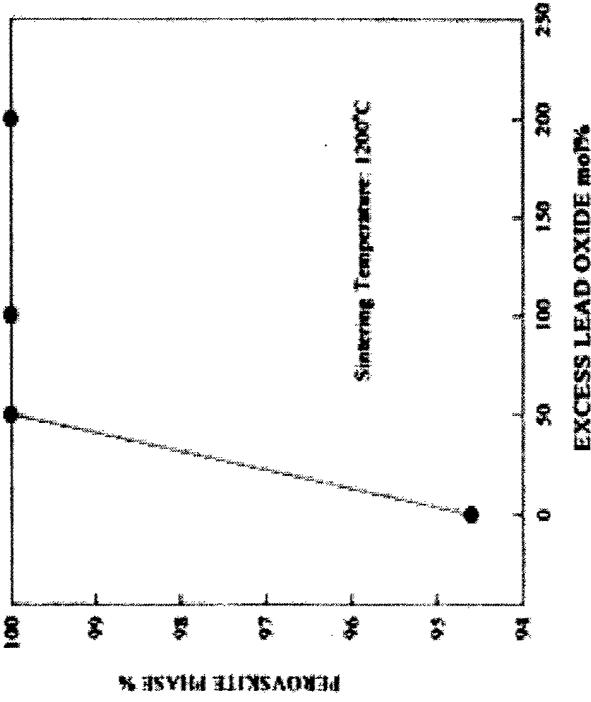
350–500°C, flux decomposition, where potassium chlorate melts at 356°C and then resolidifies to form potassium perchlorate. The potassium perchlorate is further decomposed into KCl and O<sub>2</sub> with increasing temperature [15].

750–900°C, loss of lead oxide

DTA

Endo peaks: @ 356°C melting of potassium chlorate, @ 772°C melting of KCl, @ 832°C eutectic formation between PbO-Pb<sub>3</sub>Nb<sub>2</sub>O<sub>8</sub> pyrochlore phase.

Exo peaks `@ 373°C formation of potassium perchlorate, @ 462°C formation of KCl, (= resolidification of potassium chlorate & decomposition of potassium perchlorate.)



The effect of excess lead oxide on perovskite phase formed in PMN ceramics sintered at 1200°C for 2 h.

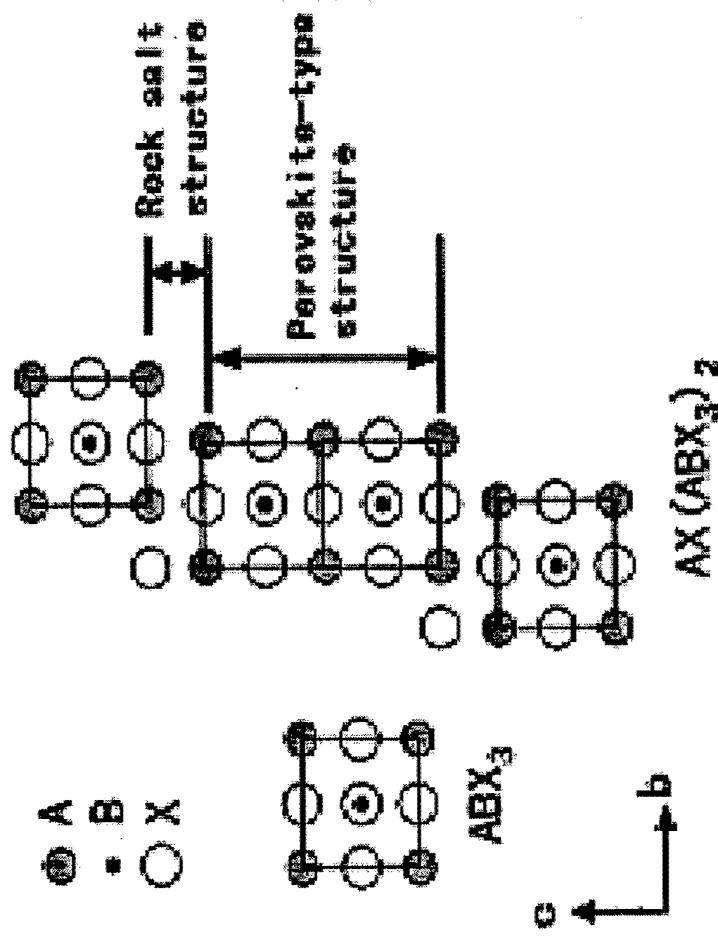
• Single phase PMN powders have been prepared in the molten salt of potassium chloride at temperatures of 900°C and above for 2 h when 100 mol % PbO excess was added in the starting composition.

- Too much excess lead oxide (e.g. 200 mol %) and a too high reaction temperature lead to the occurrence of exaggerated grain growth and the formation of faceted cubical particles, although the molten salt-derived powders exhibit litter particle agglomeration.
- The excess lead oxide enhances the formation of perovskite phase and promotes grain growth in sintered PMN ceramics, when it occurs at grain boundaries and grain junctions. This however degrades the dielectric properties of molten salt-derived PMN ceramics.

## Microcomposite particles $\text{Sr}_3\text{Ti}_2\text{O}_7\text{--SrTiO}_3$

- Microcomposite particles  $\text{Sr}_3\text{Ti}_2\text{O}_7\text{--SrTiO}_3$  with an epitaxial core–shell structure were prepared by the hydrothermal treatment of  $\text{Sr}_3\text{Ti}_2\text{O}_7$  core particles.
- The  $\text{Sr}_3\text{Ti}_2\text{O}_7$  core particles synthesized in a fused salt had a plate-like morphology with a well developed [001] plane of the Ruddlesden–Popper type crystal structure.
- The particles after hydrothermal treatment have an anisotropic morphology and a core–shell microcomposite structure: the plate-like  $\text{Sr}_3\text{Ti}_2\text{O}_7$  particles covered with  $\text{SrTiO}_3$  fine particulates and thin layers.

The  $\text{Sr}_3\text{Ti}_2\text{O}_7$  has a Ruddlesden-Popper type structure (one of layered perovskite-type structure) and plate-like particles can be synthesized with the developed [001] plane by a molten salt synthesis.



- The atomic configuration in the [001] plane of a Ruddlesden-Popper type structure is similar to that in the [001] plane of a perovskite-type structure, as schematically shown.
- Especially, the lattice mismatch between  $\text{Sr}_3\text{Ti}_2\text{O}_7$  and  $\text{SrTiO}_3$  is only 0.1%, which suggests the possible formation of  $\text{SrTiO}_3$  on the developed surface of  $\text{Sr}_3\text{Ti}_2\text{O}_7$  with epitaxy.

The plate-like particles have a smooth and well-developed rectangular plane with a side length of 20–30 nm and an aspect ratio (side length / thickness) of about 10.

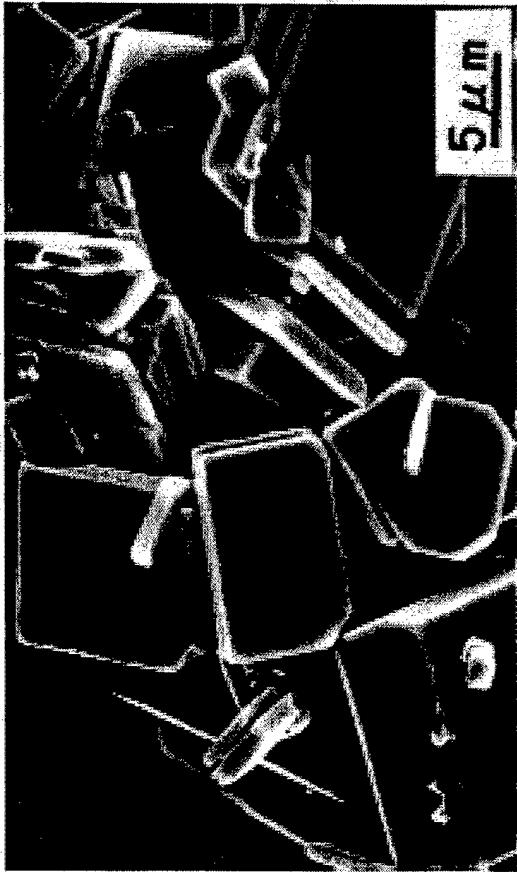


Plate-like  $\text{Sr}_3\text{Ti}_2\text{O}_7$  core particles prepared by molten salt synthesis.

•  $\text{SrCO}_3$  and  $\text{TiO}_2$  (3:2 molar ratio) mixed for 24 h in ethanol with media of zirconia balls. The slurry was dried and then an equal weight of salts (50 mol %  $\text{KCl}$  and 50 mol %  $\text{NaCl}$ ) was mixed with the dried powder by a mortar and pestle for 30 min.

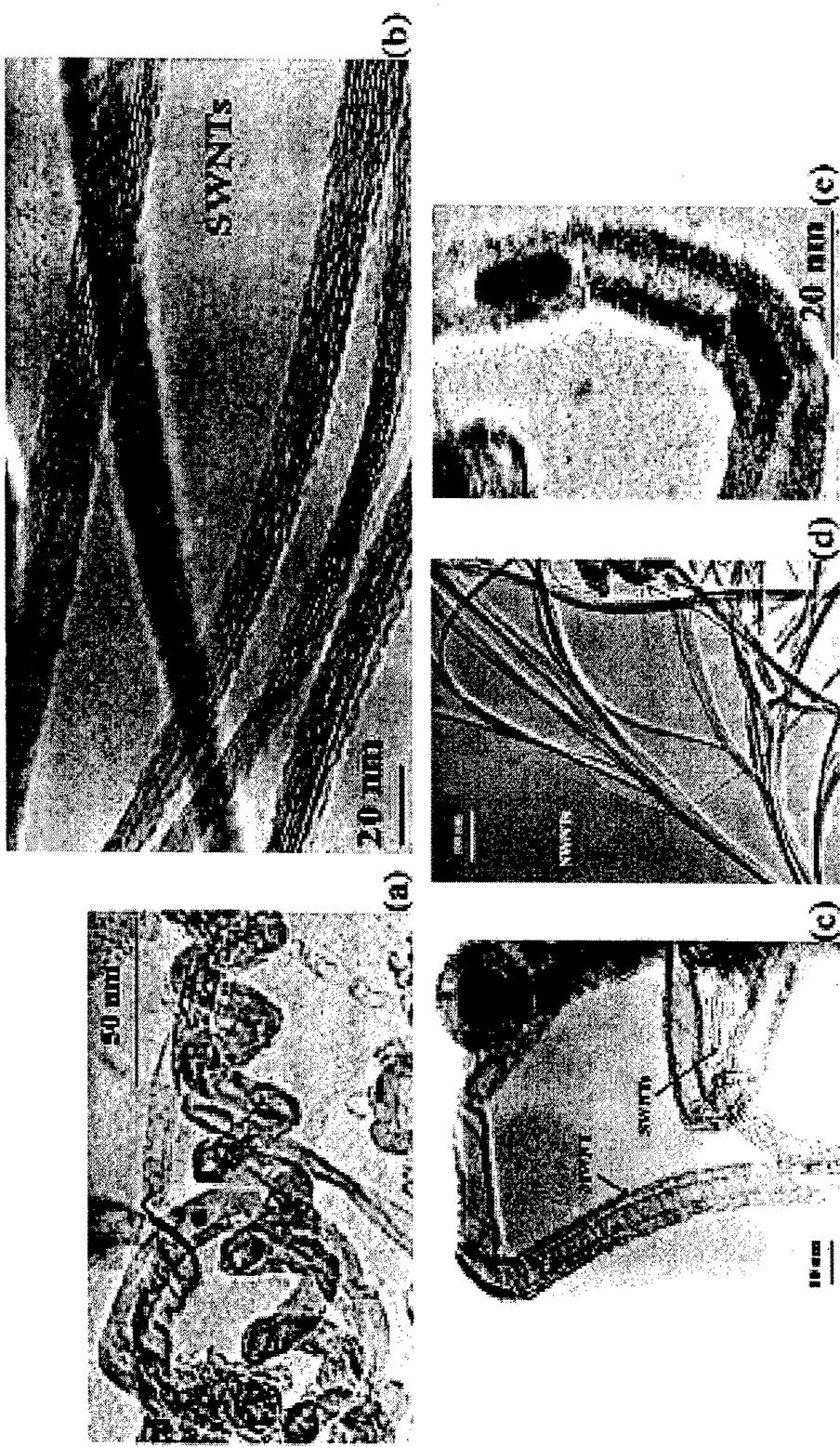
• The mixture was heated in a Pt crucible at 1200°C for 8 h and cooled in air.

• The products were washed with hot deionized water several times in order to remove the salts.

## Synthesis of SWNTs and MWNTs by a molten salt method

- Method to obtain the single-walled and multi-walled carbon nanotubes
- Electrolytic conversion of graphite to carbon nanotubes in fused NaCl at 810 °C.
- Filling of the nanotubes is also possible if elements are added in the salt solution.

TEM imaging of the various morphologies of nanotubes.



**PROCESSING, MICROSTRUCTURE AND MECHANICAL BEHAVIOR  
OF DIRECTIONALLY-SOLIDIFIED EUTECTIC CERAMIC OXIDES**

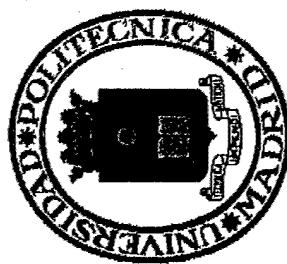
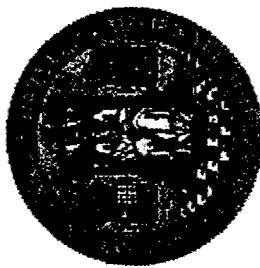
**V. M. Orera, J. I. Peña, R. I. Merino, A. Larrea,  
J. Llorca, J. Y. Pastor, P. Poza,  
J. Martínez, A. Ramírez, M. López, J. Quispe**



Institute of Materials Science of Aragon  
Universidad of Zaragoza / CSIC

Department of Materials Science  
Polytechnic University of Madrid

Department of Physics of Condensed Matter  
University of Seville

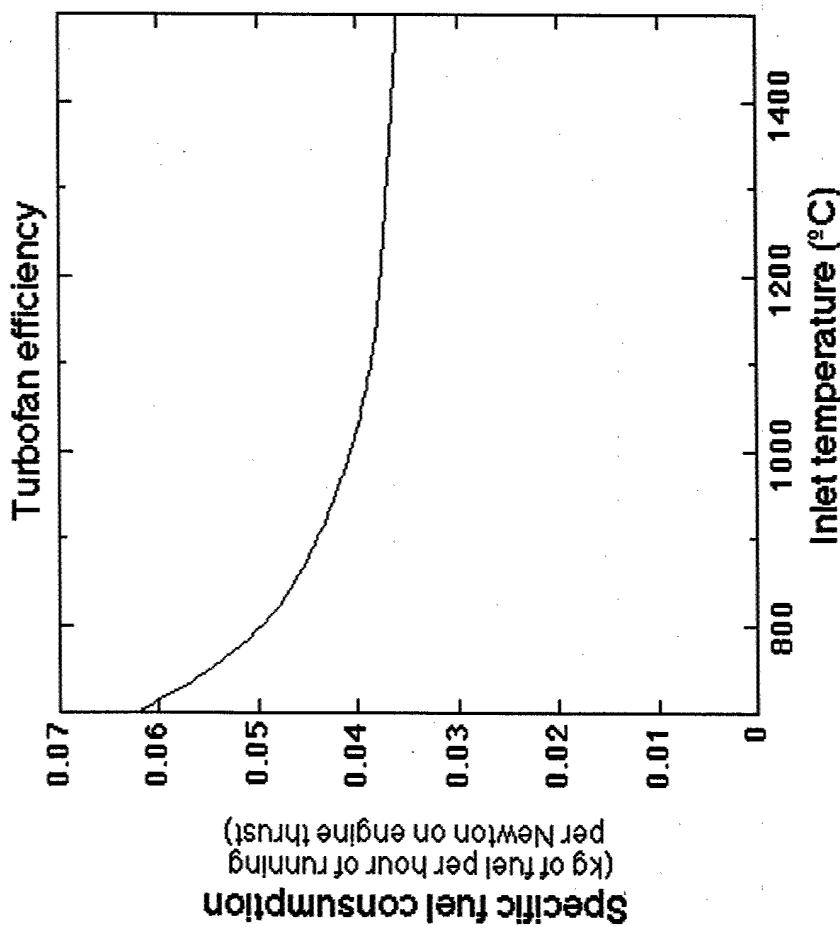
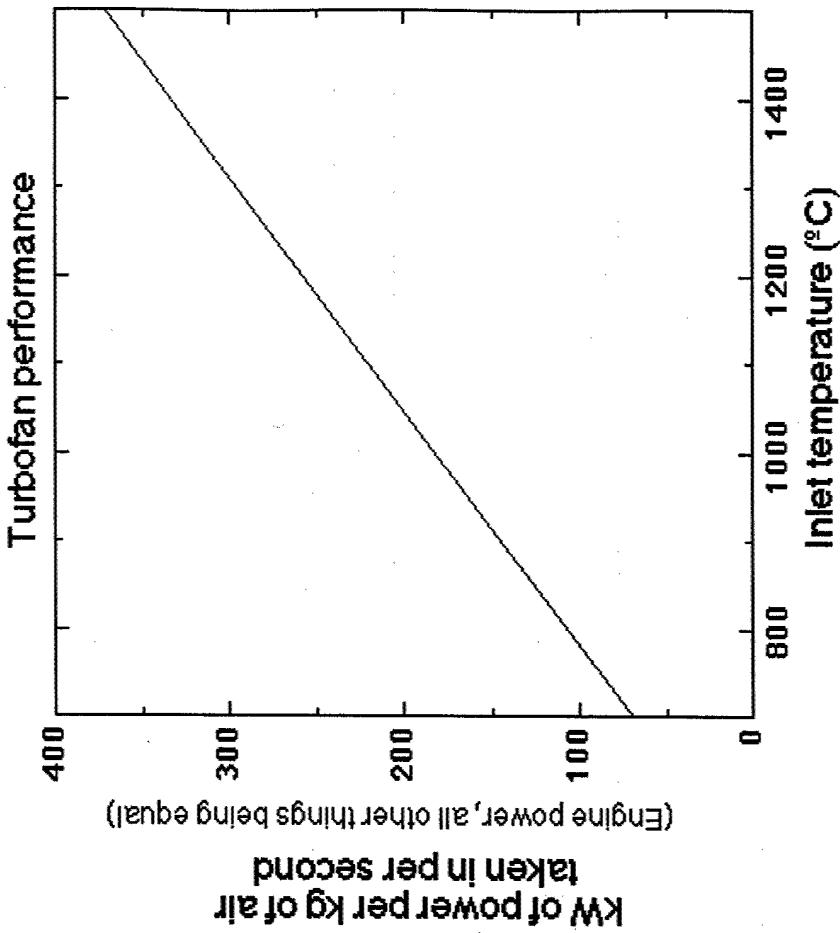


# OUTLINE

- Motivation and Introduction
- Processing
- Microstructure
  - Morphology
  - Phase distribution & composition
- Residual stresses
  - Experimental results
  - Stress generation and relaxation
- Microstructure stability
- Mechanical behavior
  - Ambient temperature properties
  - Toughening mechanisms
  - High temperature strength
- Conclusions

## Why structural materials for high temperature?

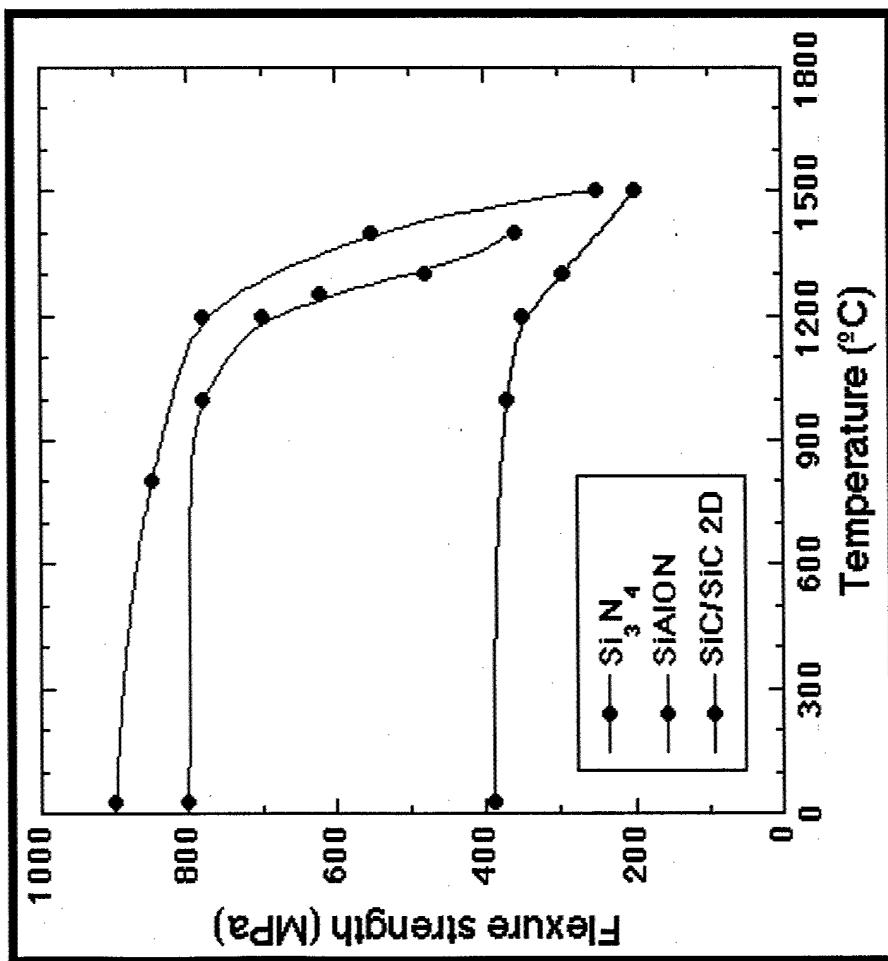
- Higher temperatures in thermal engines lead to
  - Better efficiency and performance
  - Cleaner emissions



## **Basic requirements for high temperature structural materials**

- High melting point
- Mechanical properties
- Microstructure stability
- Oxidation resistance

**SiC- and  $\text{Si}_3\text{N}_4$ -based  
ceramics undergo severe  
oxidation above 1400°C**



## **Directionally-solidified eutectic oxides**

- Eutectic composites
  - Fine microstructure
  - Excellent bonding between phases
  - Clean interface
  - Stable up to near the eutectic temperature
- Directional solidification
  - Composite highly textured along growth direction
  - Oxides
  - Chemically stable in oxidizing environments

***The best mechanical properties have been obtained so far in the  $Al_2O_3/c-ZrO_2(Y_2O_3)$  system.***

***Flexure strength > 1.1 GPa, toughness = 7.8 MPa m<sup>1/2</sup>***

## History

1970-1980 1 <600MPa at RT but good retention up to 1850K (524 MPa)

1990-1995<sup>2-5</sup> 1.0-1.5 GPa at RT

1995- Sayir et al.<sup>6</sup> found tensile strength from 1.2 GPa at RT to  
800 MPa at 1673K

<sup>1</sup> C.O. Hulse and J.A. Batt UARL N910803, (1974)

<sup>2</sup> V.A. Borodin et al. J. Cryst. Growth 104 (1990) 148

<sup>3</sup> J. Hommeny & J.J. Nick, Mater. Sci. Eng. A117 (1990) 123

<sup>4</sup> H. E. Bates, Ceram. Eng. Sci. Proc. 13 (1992) 190

<sup>5</sup> E. L. Courtright et al. Ceram. Eng. Sci. Proc. 14 (1993) 671

<sup>6</sup> A. Sayir & S.C. Farmer, Acta Mater 48, 4691-7 (2000)

**Objective: Production of melt growth composites  $Al_2O_3$  -  $ZrO_2(Y_2O_3)$  with optimized mechanical properties**

- Study of the mechanical properties:  
Flexural and compressive strength & toughness.  
Retention at high T

Focus on

- Processing (Microstructure)

Growth rate: 10- 1500mm/h

Rotation 200 to 0 rpm

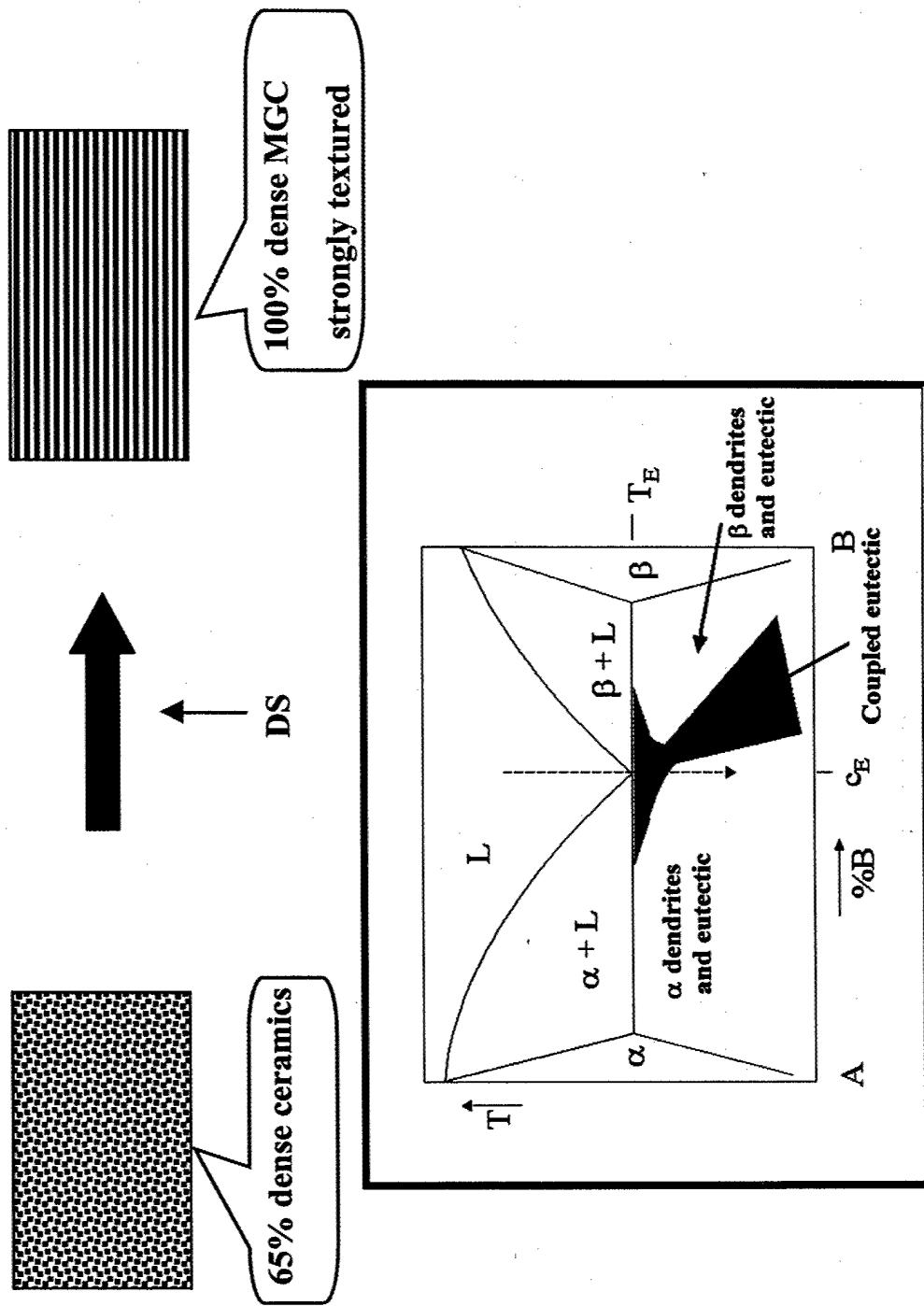
- Influence of the  $Y_2O_3$  amount in the zirconia phase

From the  $Al_2O_3$ - $ZrO_2$  eutectic to the  $Al_2O_3$ - $ZrO_2$ - $Y_2O_3$  peritectic,  $Y_2O_3$  content,  $Y=0$  to 12.2% (mol  $Y_2O_3$  / mol  $ZrO_2 + Y_2O_3$ )

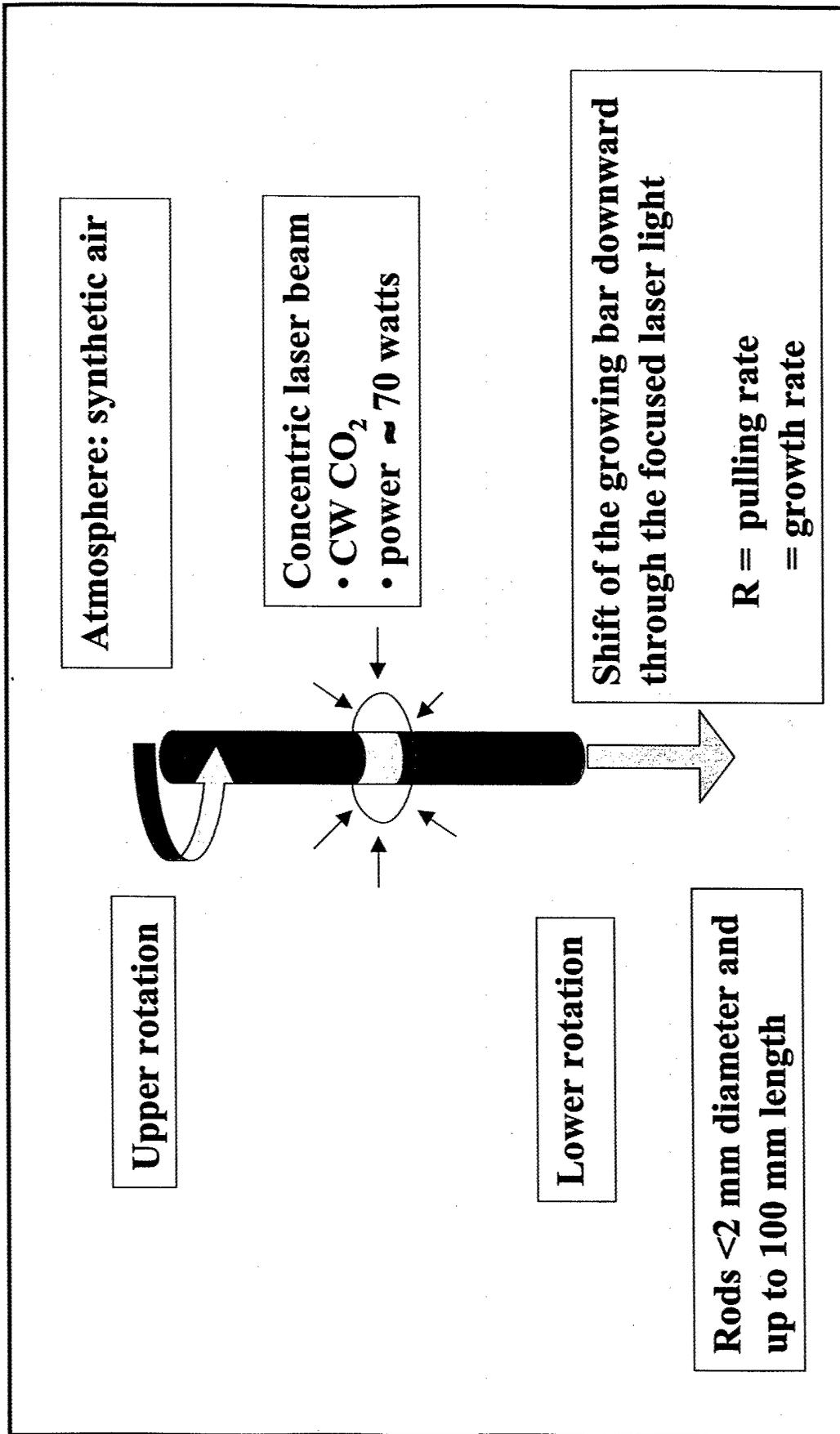
- Role of the thermo-elastic residual stresses

## Preparation Procedures:

Melt Grown Composites (MGC) using Directional Solidification (DS)



## Laser Heated Float Zone: $T_E = 1860^\circ C$



## **Conciliate the mechanical measurements size needs with the growth constraints**

- Flexural strength rods  $\approx$  1 mm diameter
- Compression experiments & toughness  $>$  2mm
- High axial thermal gradients  $\longrightarrow$  Large radial gradients  $\longrightarrow$  cracks more frequent in bars with larger radius

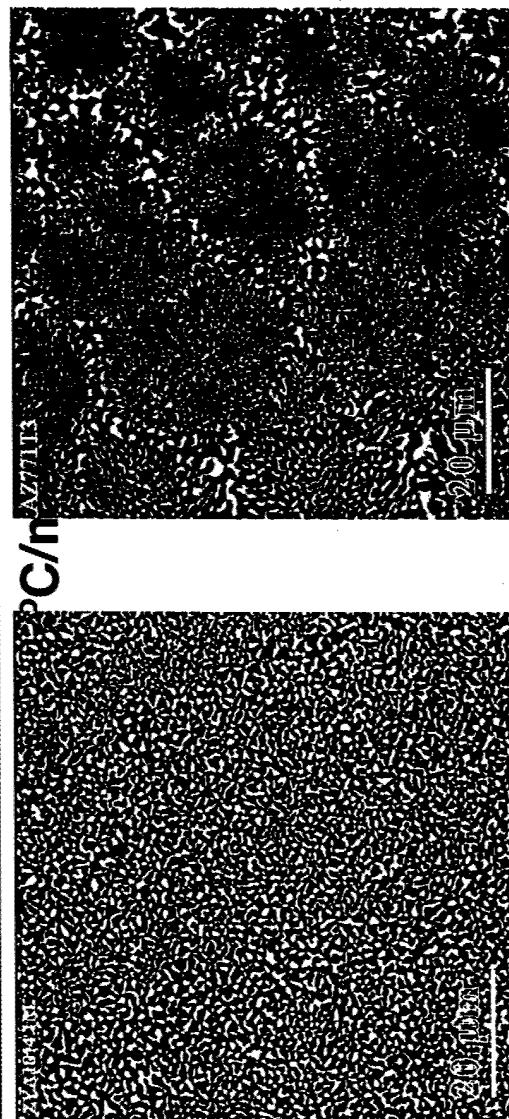
High speed rotation induces melt homogeneity and decreases lateral gradient effects but it is problematic for narrow samples

### **Conclusion:**

None or low speed rotation (banding) for samples around 1mm  
and 200 rpm precursor rotation for larger samples

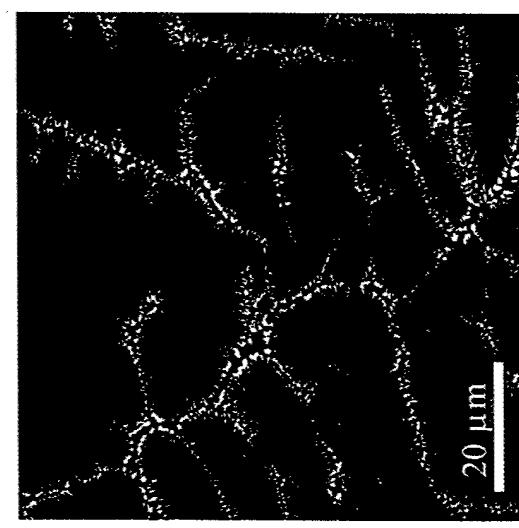
## $Al_2O_3/c-ZrO_2(Y_2O_3)$ eutectic

Microstructure versus solidification rate.  $G \approx 600$

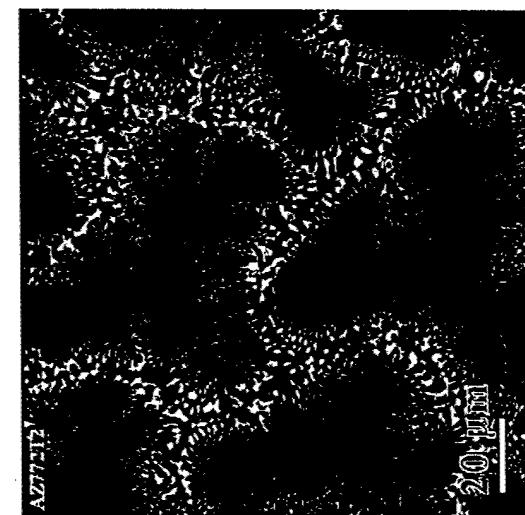


$R = 10 \text{ mm/h}$

$R = 100 \text{ mm/h}$



Transverse



$R = 300 \text{ mm/h}$

### **Samples with colony structure**

It was induced at  $R > 30$  mm/h as the  $\text{Al}_2\text{O}_3$  phase leads the growth due to its high entropy of fusion ( $\Delta S = 5.7\text{R}$ ).

Composition

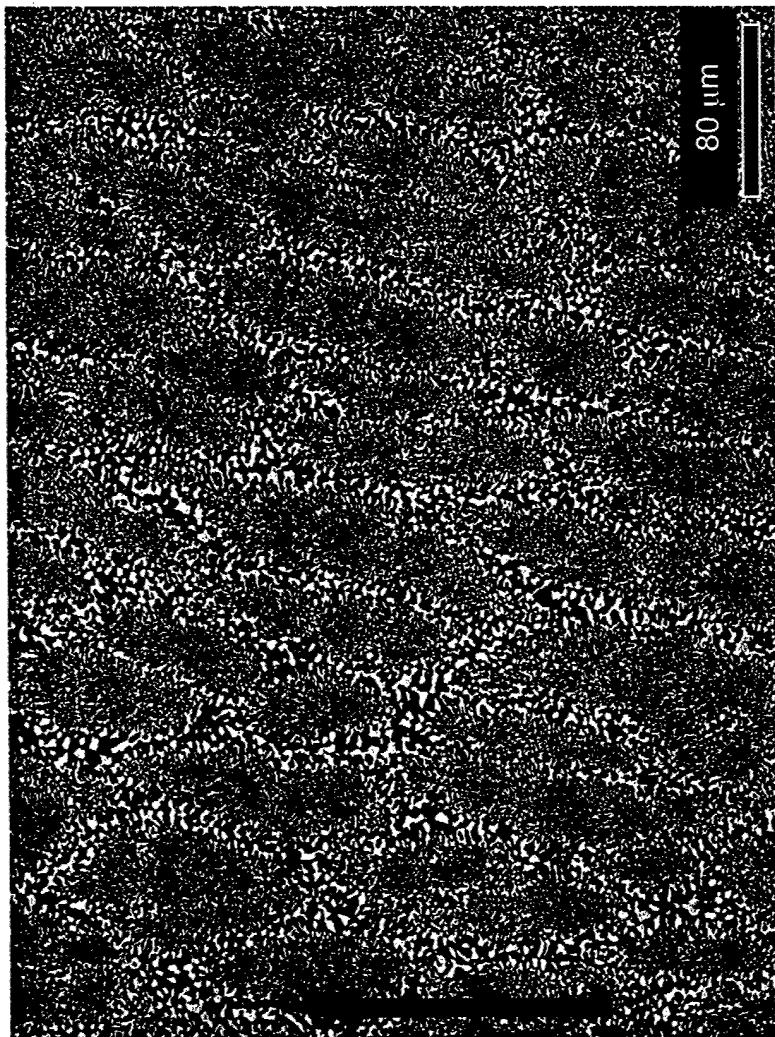
$$\alpha\text{-Al}_2\text{O}_3 \approx 70\% \text{ vol.}$$
$$\text{ZrO}_2(\text{Y}_2\text{O}_3) \approx 30\% \text{ vol.}$$

Colonies

Diameter  $31 \pm 10 \text{ } \mu\text{m}$

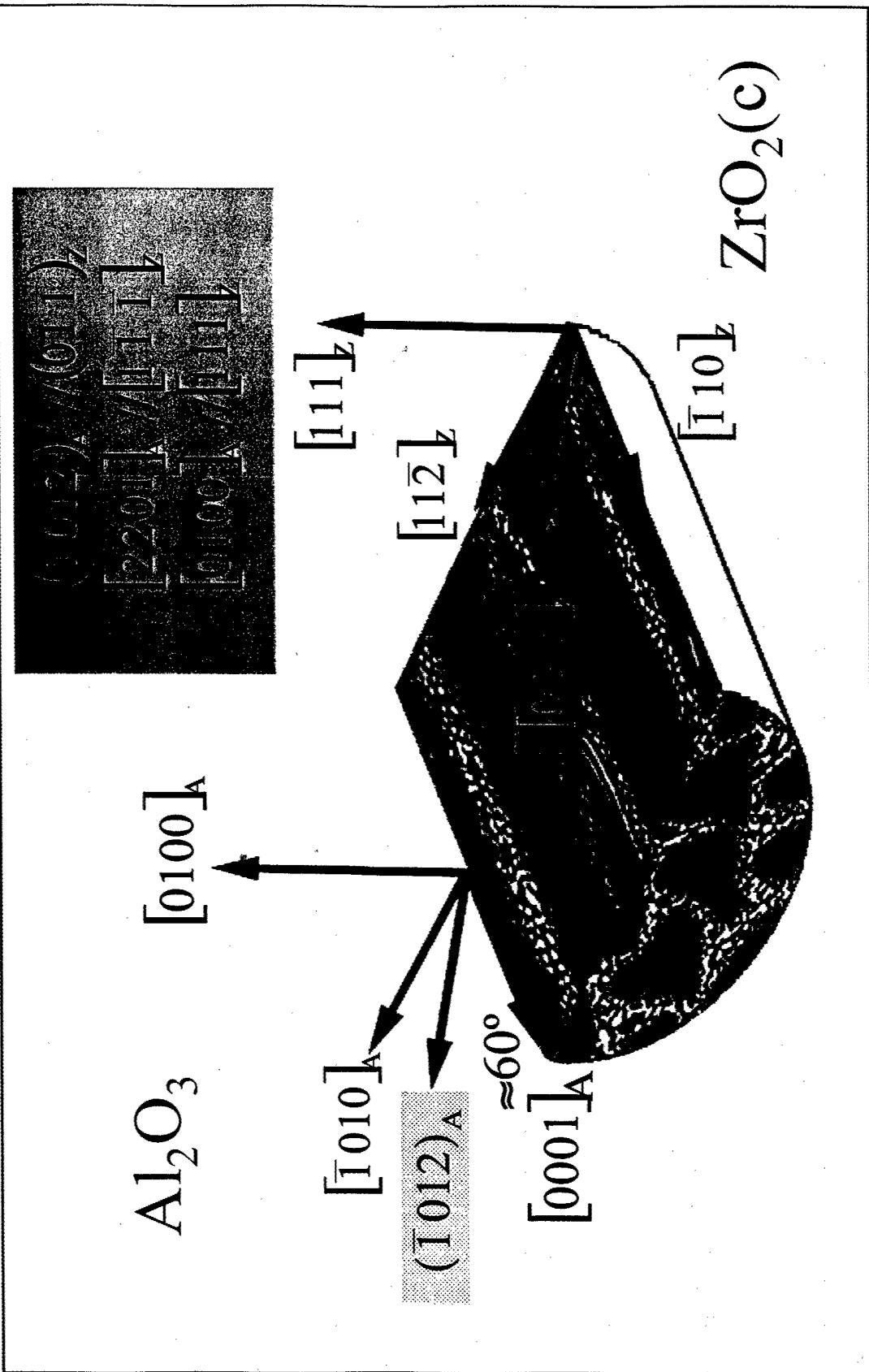
Aspect ratio  $\approx 3$

Colony boundary  $13 \pm 4 \text{ } \mu\text{m}$



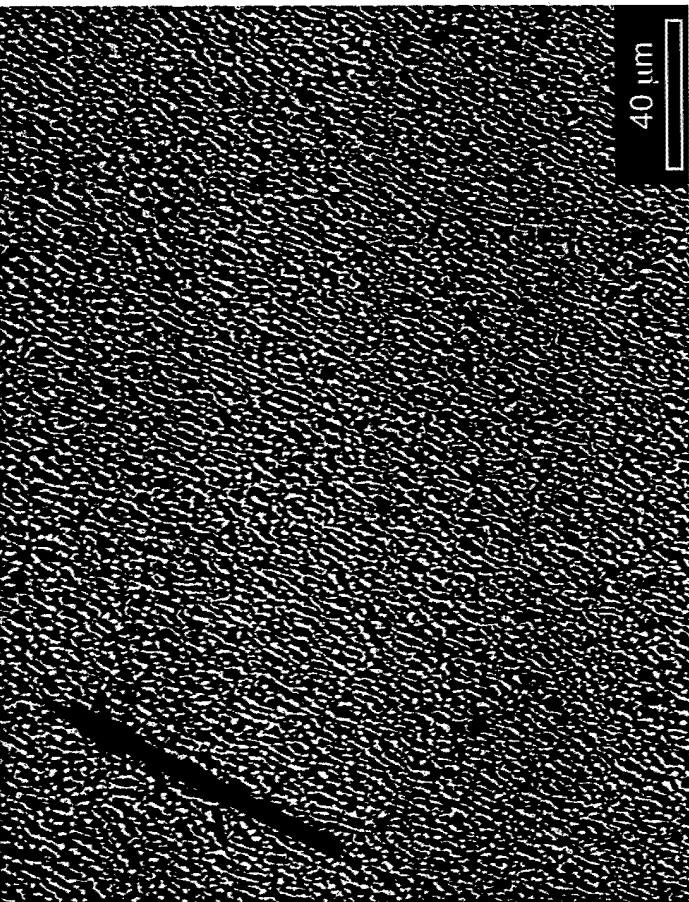
**Longitudinal**

## $Al_2O_3/c$ - $ZrO_2(c)$ Crystallographic orientation relationships



***Interpenetrating structure:***  
**Highly homogeneous 3d network**

It was induced at  $V = 10 \text{ mm/h}$  by the coupled growth of both phases ( $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$ )

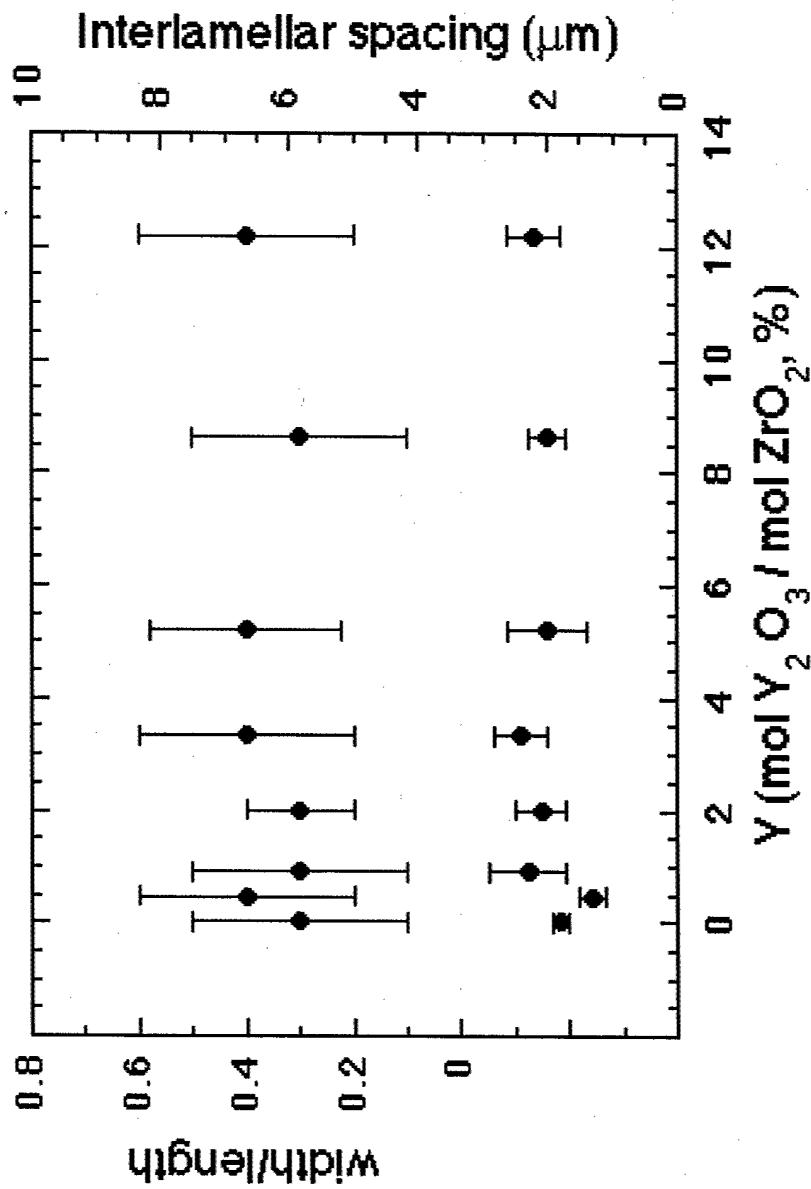


Composition  
 $\alpha\text{-Al}_2\text{O}_3 \approx 70\% \text{ vol.}$   
 $\text{ZrO}_2(\text{Y}_2\text{O}_3) \approx 30\% \text{ vol.}$

Fine dispersion of  $\text{ZrO}_2(\text{Y}_2\text{O}_3)$  platelets embedded into the  $\text{Al}_2\text{O}_3$  matrix

### Interpenetrating structure

Aspect ratio and interlamellar spacing



## Composition

## *Influence of the $Y_2O_3$ amount in the zirconia phase*

From the  $\text{Al}_2\text{O}_3\text{-ZrO}_2$  eutectic to the  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-Y}_2\text{O}_3$  peritectic,  $\text{Y}_2\text{O}_3$  content,  $Y = 0$  to 12.2% (mol  $\text{Y}_2\text{O}_3$  / mol  $\text{ZrO}_2 + \text{Y}_2\text{O}_3$ )

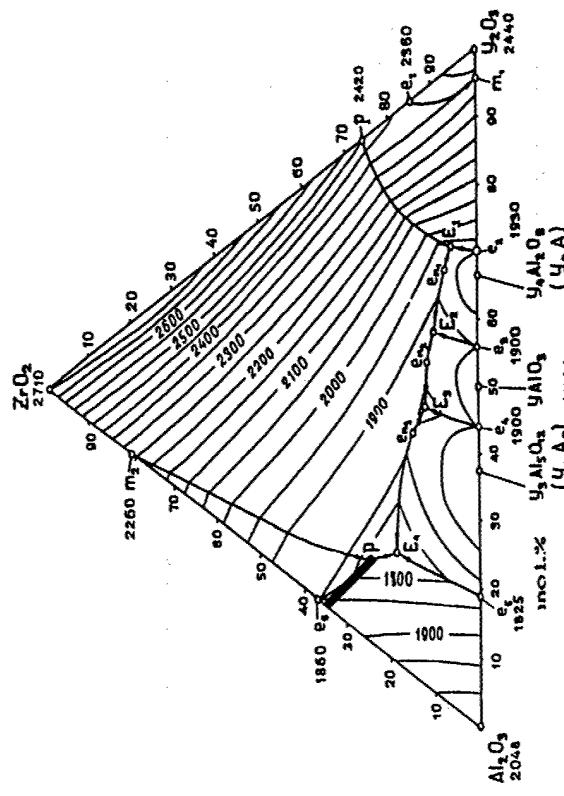
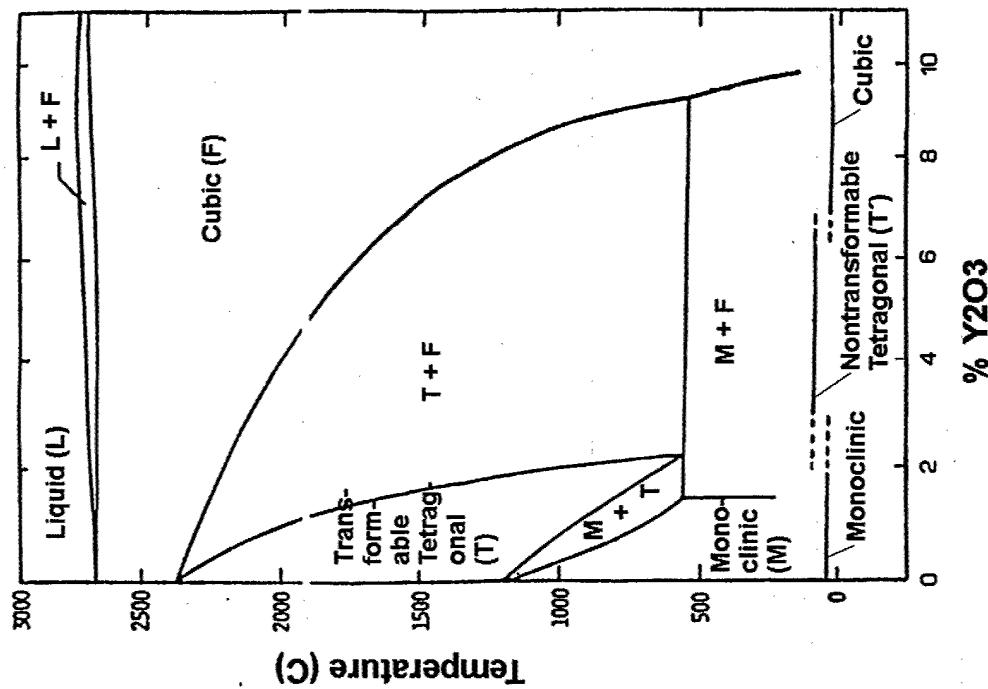
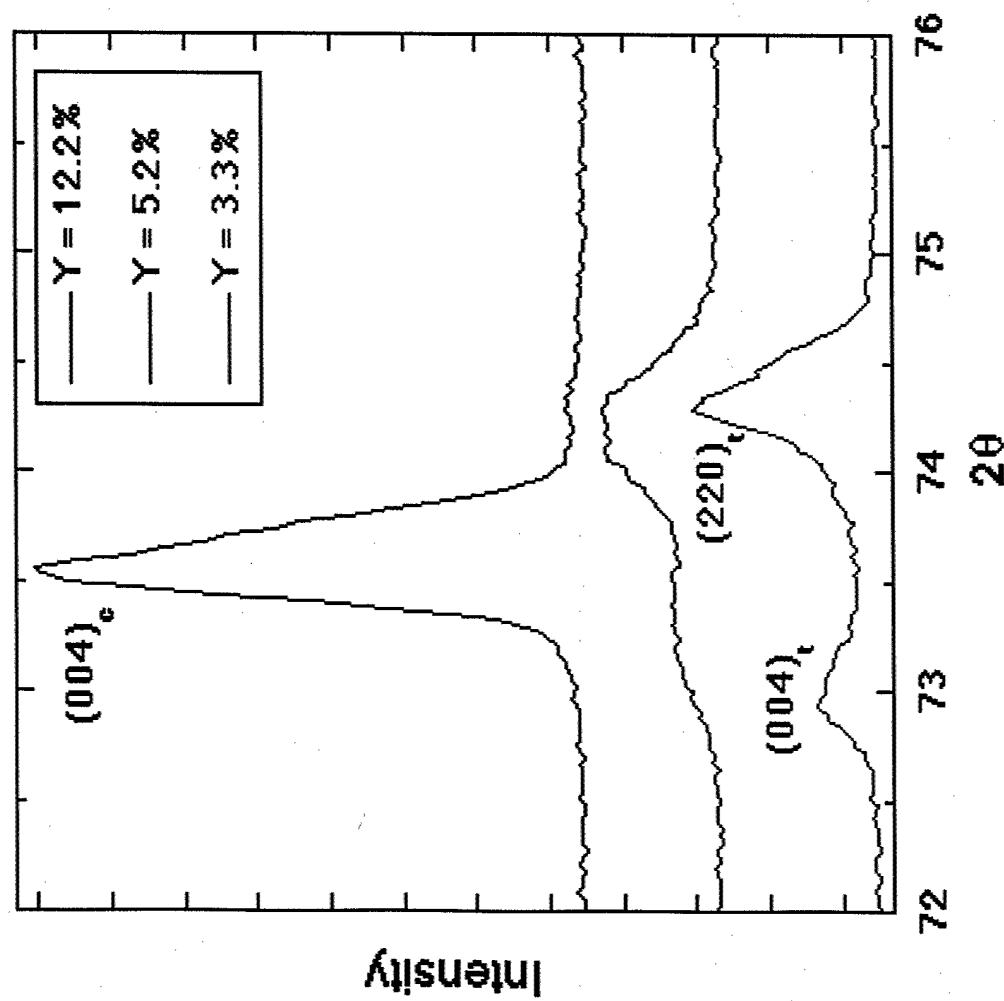


Fig. 5. Projection of the liquidus surface for the system  $\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-Y}_2\text{O}_3$ .

***ZrO<sub>2</sub> phase volume fraction***  
**X-ray diffraction**

X-ray diffraction peaks



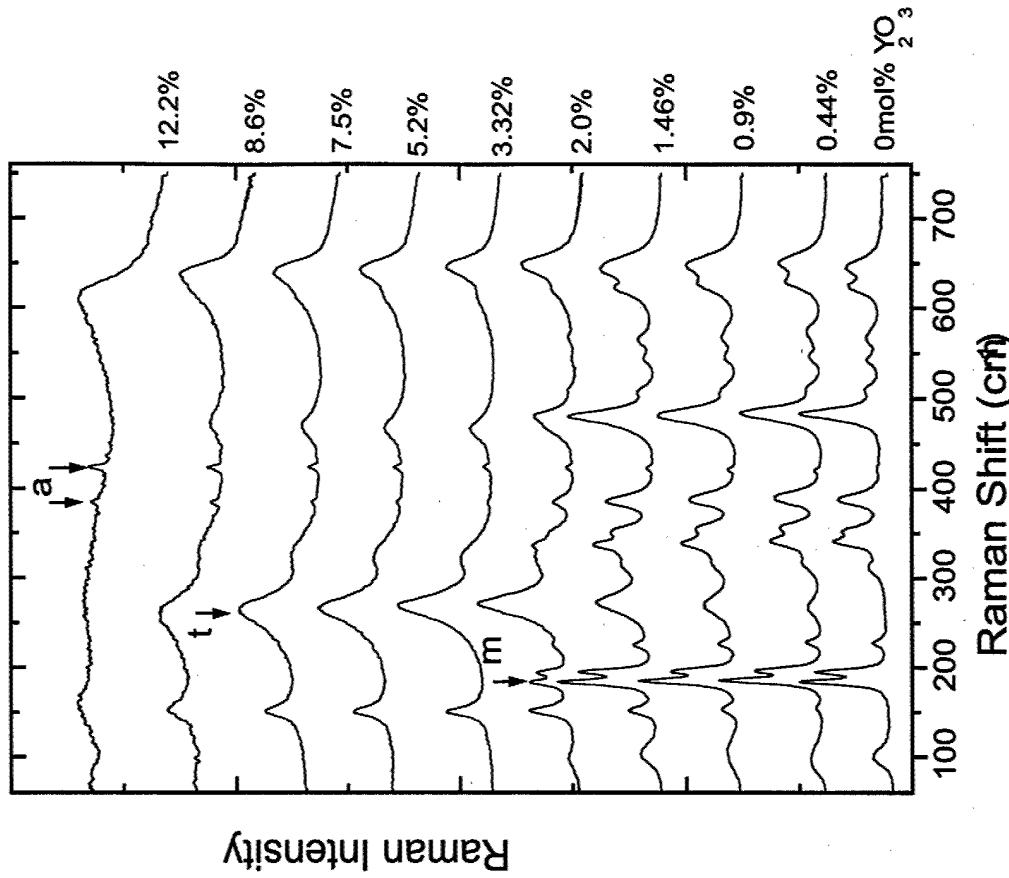
X-ray diffraction showed that the  $c/a$  ratio of (t)  $\text{ZrO}_2$  decreased with  $\gamma$

Non-transformable (t') and (t'')  $\text{ZrO}_2$  phases are present

## $ZrO_2$ phase volume fraction

### Raman spectroscopy

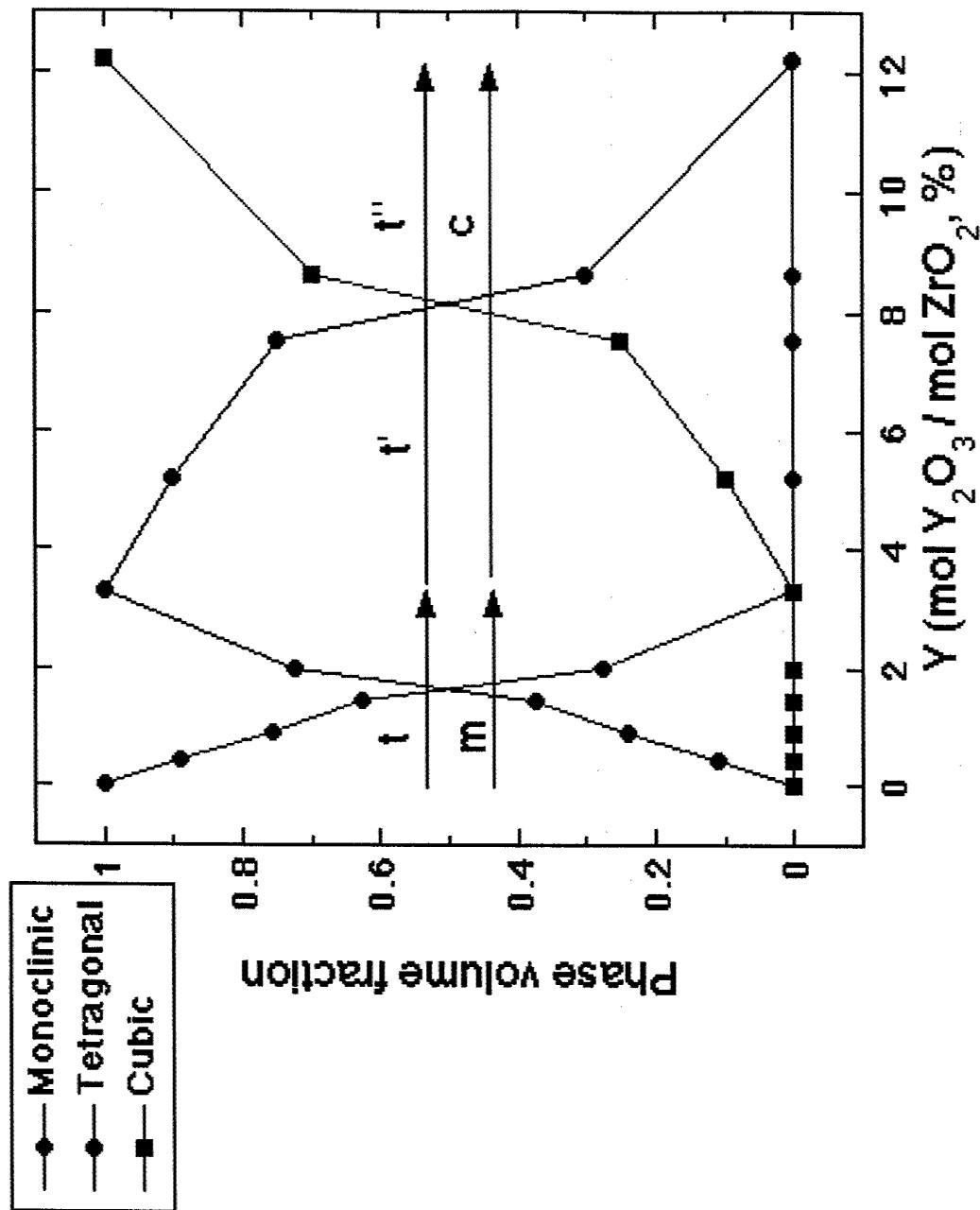
$$Y > 3.3\%$$
$$X_c + X_t = 1$$
$$X_t = I_{260} / I_{260}(Y=3.3)$$



$$Y < 3.3\%$$
$$X_m + X_t = 1$$
$$X_t / X_m = I_{260} / 1.8 I_{177}$$

## $ZrO_2$ phases

### $ZrO_2$ phase volume fraction



## Piezo-spectroscopy of R1 and R2 lines in $Al_2O_3$

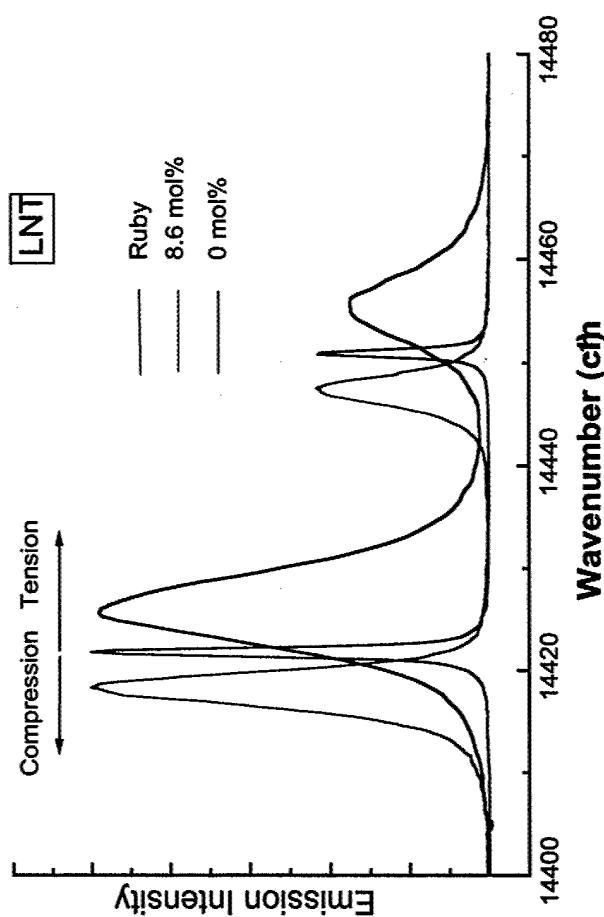
Residual stresses in  $Al_2O_3$  can be computed from the shift in R1 and R2 peaks using the piezospectroscopic tensors in ruby.

$$\Delta R_1(\text{cm}^{-1}) = 3.26(\sigma_{11} + \sigma_{22}) + 1.53 \sigma_{33}$$

$$\Delta R_2(\text{cm}^{-1}) = 2.73(\sigma_{11} + \sigma_{22}) + 2.16 \sigma_{33}$$

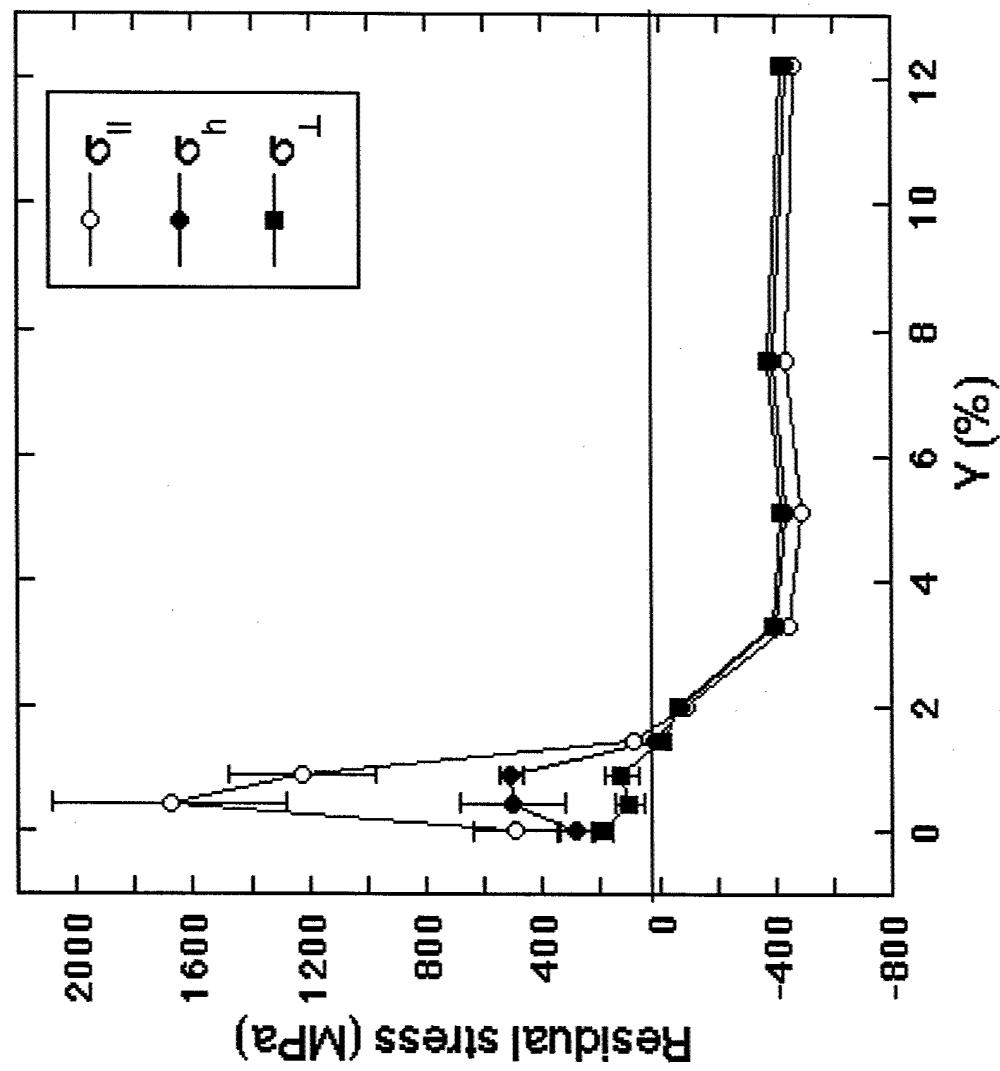
( $\sigma$  in GPa)

- Assumptions
  - The alumina c-axis is parallel to the rod axis.
  - The piezospectroscopic effect is isotropic in the alumina basal plane.
  - the stress state in the eutectic is transversally isotropic

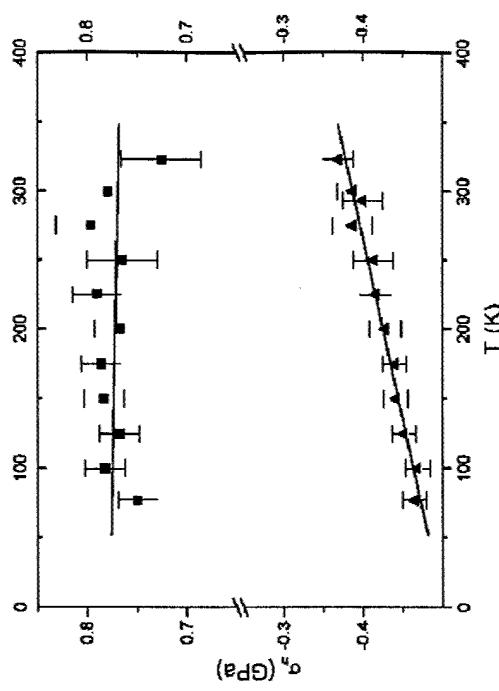


## Residual stresses at ambient temperature

Interpenetrating structure

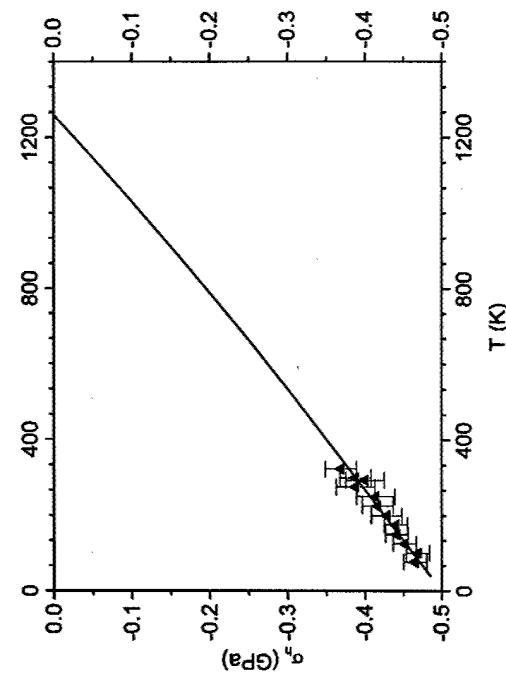


## Residual stresses as a function of temperature



Hydrostatic residual stresses in the alumina phase vs temperature

- AZE with Monoclinic zirconia, Martensitic
- ▲ AZE with "c" or "f" zirconia, Thermo-elastic



Thermo-elastic stresses depend on the CTE misfit,  $T_0$  stress free temperature and  $K^*$  an effective elastic modulus

$$\sigma(T) = K^* \epsilon(T) = K^* \int_T^{T_0} (\dot{\alpha}_A - \dot{\alpha}_Z) dT$$

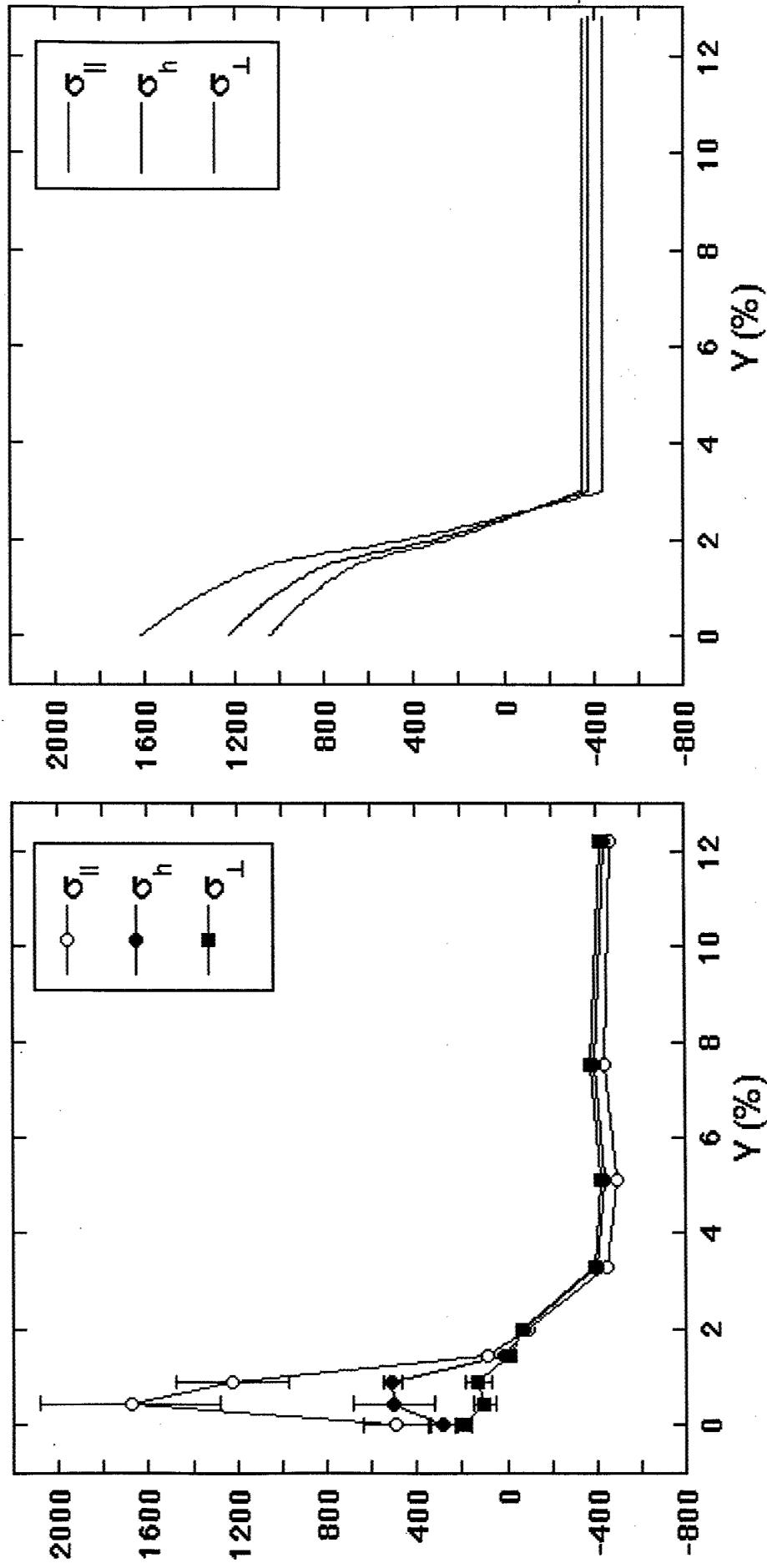
with  $\alpha_A - \alpha_Z = -3.15 \times 10^{-6} + 1 \times 10^{-10} T - 5.5 \times 10^{-13} T^2$   
 $T_0 = 1270 \pm 35 \text{ K}$ ,  $K^* = 118 \pm 2.7 \text{ GPa}$  in  
agreement with a model of spherical  $\text{ZrO}_2$  particles in a  $\text{Al}_2\text{O}_3$  matrix (9.5 GPa)

## ***Self-consistent modeling***

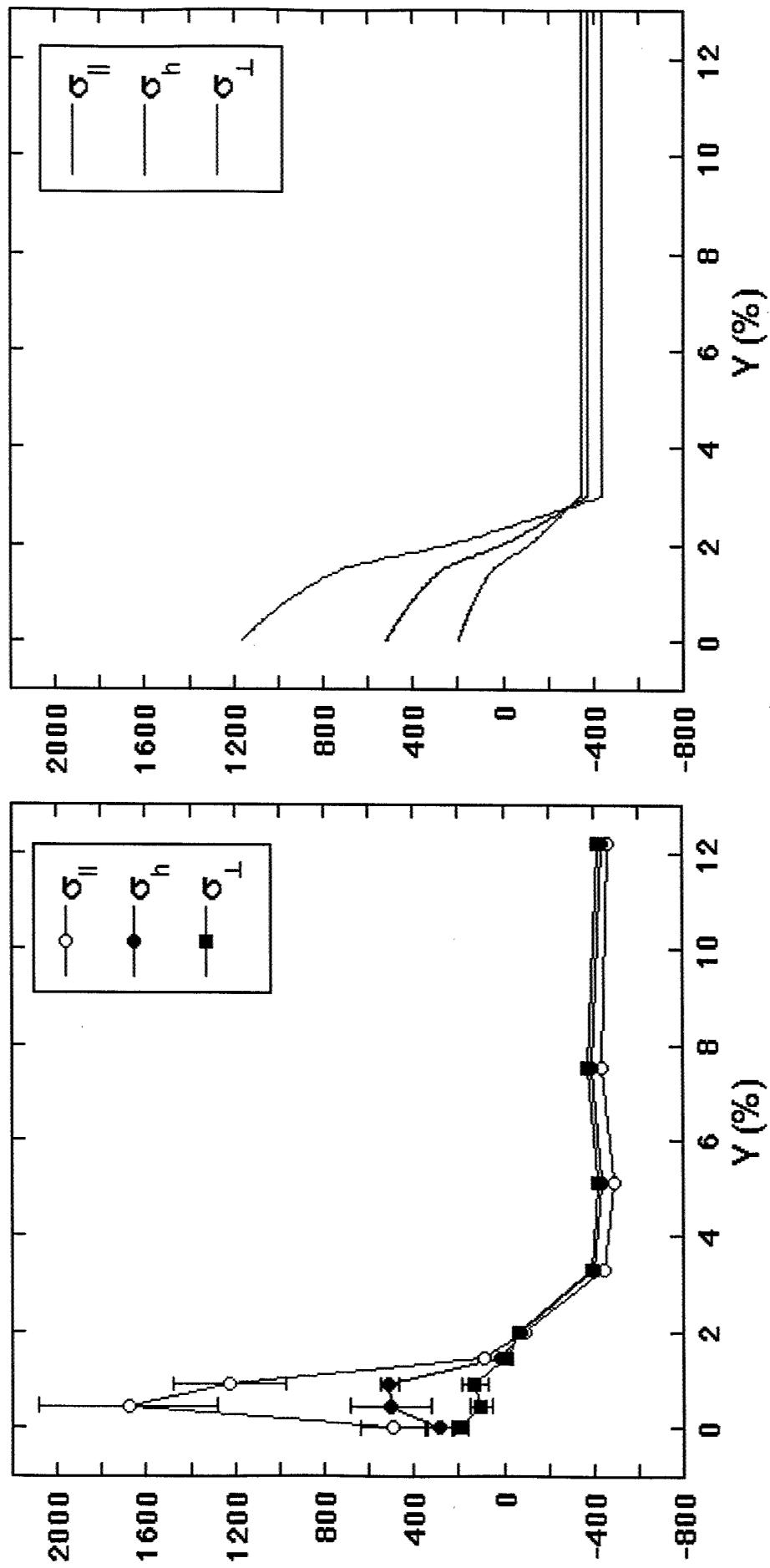
### **Hypotheses**

- Alumina matrix: Transversally isotropic solid  
c-axis parallel to the rod axis  
 $\alpha_a = 9.2 \cdot 10^{-6} \text{ K}^{-1}$  (c axis, average from 0 to 1000°C))  
 $\alpha_a = 8.0 \cdot 10^{-6} \text{ K}^{-1}$  (m/a axis)
- Zirconia inclusions:  
Randomly distributed ellipsoids aligned in the rod axis  
Aspect ratio  $\approx 3$   
Isotropic, same elastic constants for **m**, **t**, and **c** phases  
 $\alpha_m = 7.5 \cdot 10^{-6} \text{ K}^{-1}$   
 $\alpha_c = \alpha_t = 12.65 \cdot 10^{-6} \text{ K}^{-1}$   
**t**  $\rightarrow$  **m** transformation at 950 °C ( $\Delta V = 4.67\%$ )
- Stress free temperature: 1150 °C

**Comparison with experiments**  
**No stress relaxation**

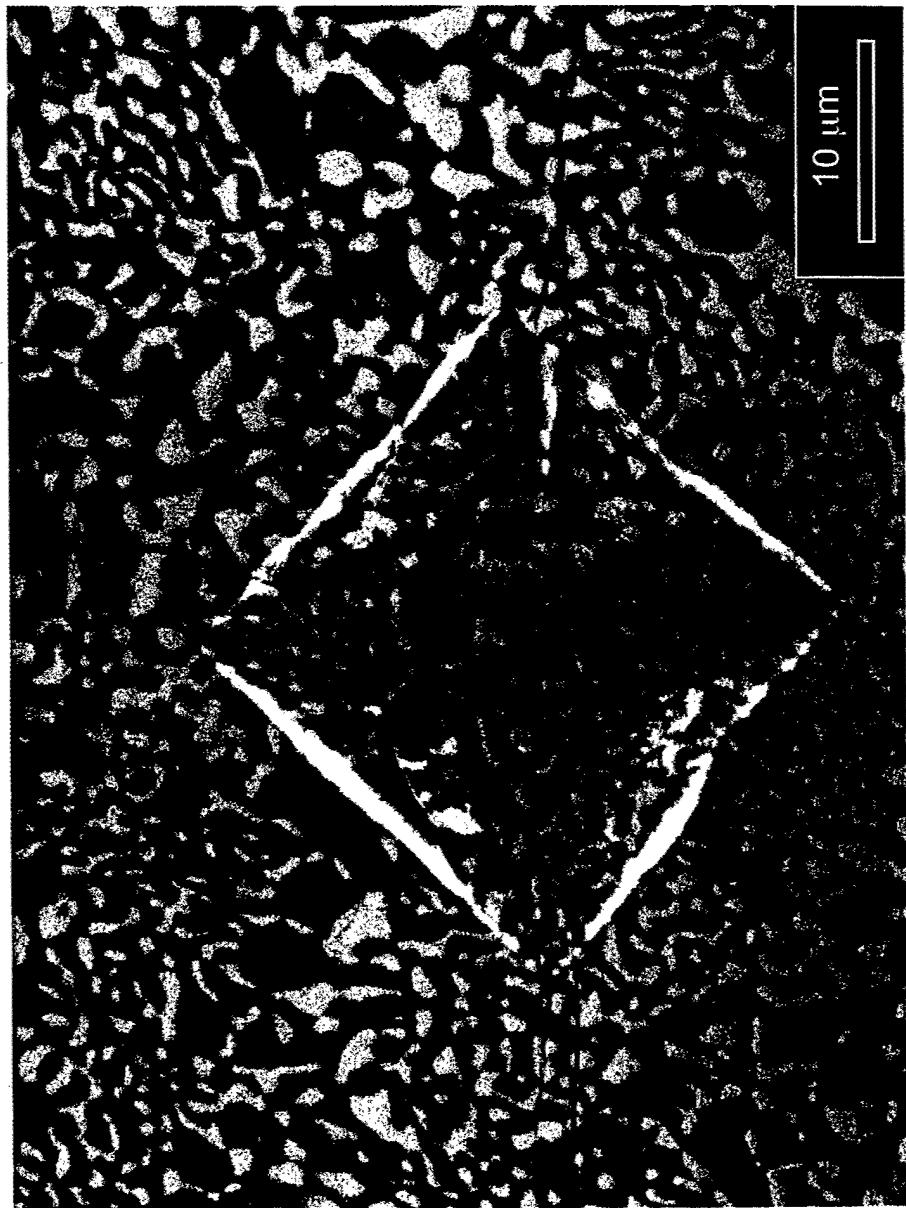


**Comparison with experiments**  
stress relaxation in the  $\text{Al}_2\text{O}_3$  basal plane



## **Toughening mechanisms**

$\gamma = 10\%$



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## ***Toughening mechanisms***

### Crack arrest and overlapping



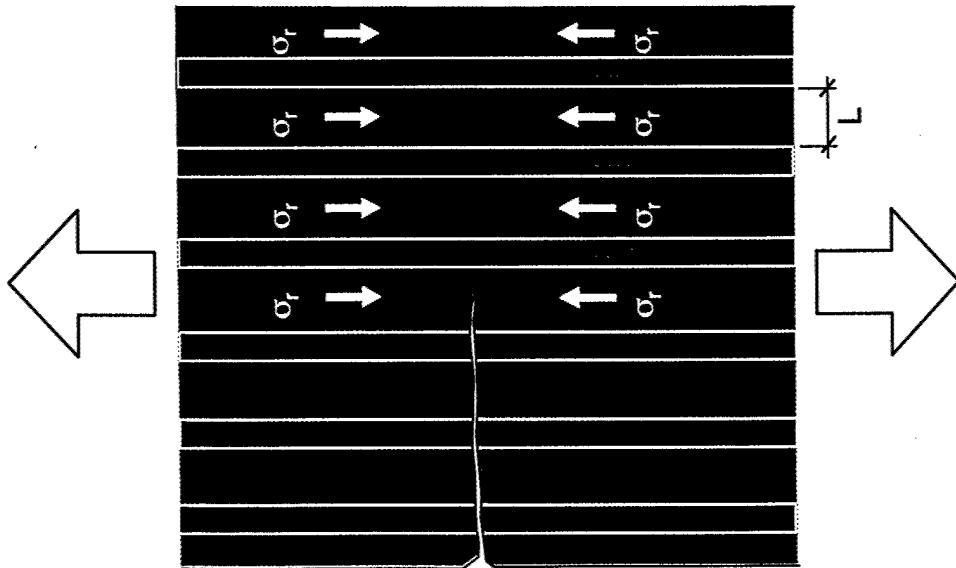
#### Causes

- Phases and interfaces with different crack growth resistance.
- Compressive residual stresses in  $\text{Al}_2\text{O}_3$ .

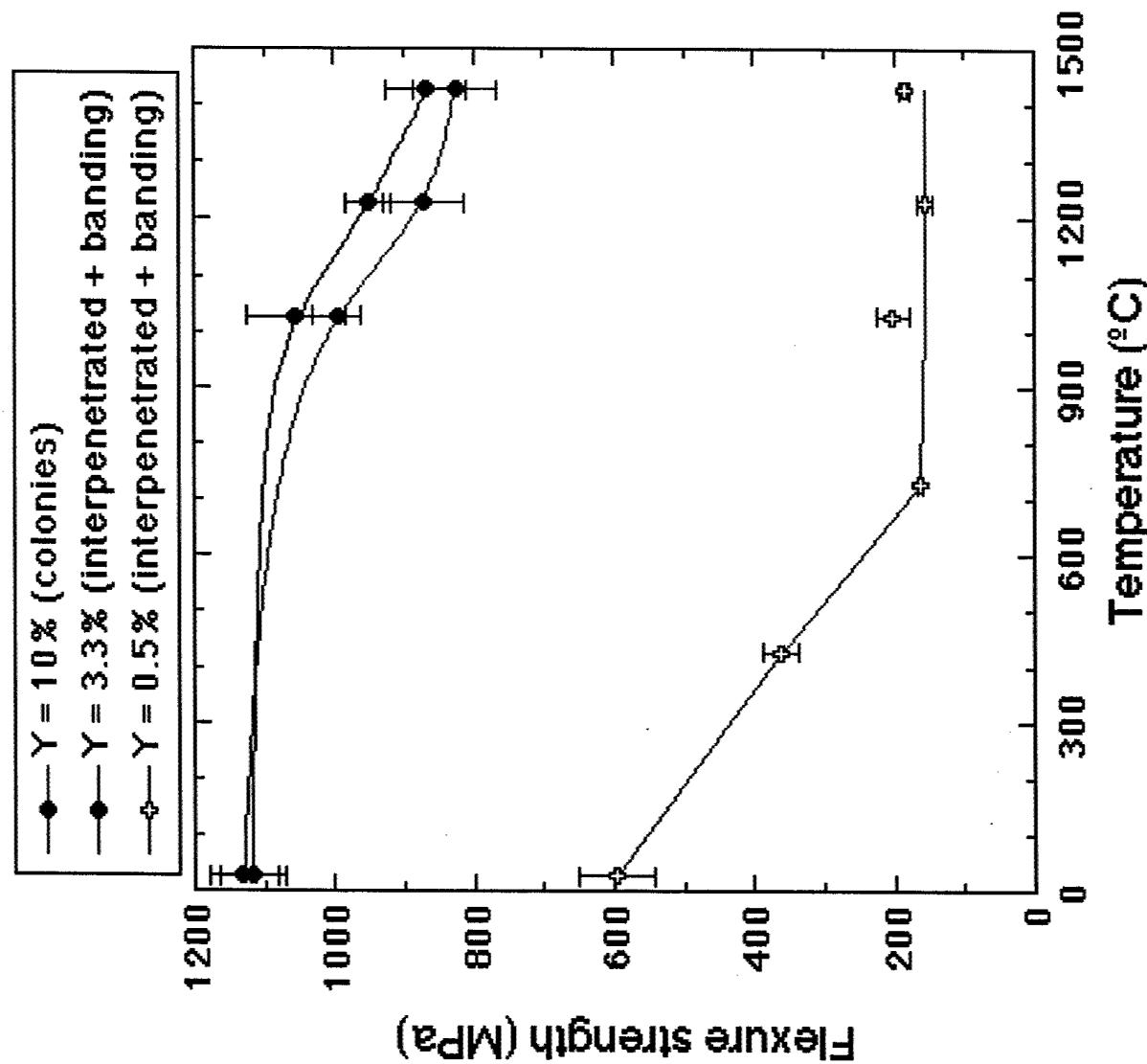
## Toughening mechanisms

### Effect of residual stresses

$$\Delta K_C = 2\sigma_r \sqrt{\frac{2L}{\pi}} = 1.6 \text{ MPa}\sqrt{\text{m}}$$
$$\sigma_r = 450 \text{ MPa}, L = 5 \mu\text{m}$$



## Mechanical behavior



## ***High temperature flexure strength***

### Mechanisms of strength reduction

$\gamma = 3.3\%$

- No changes in microstructure or critical defects
- Release of residual stresses  $\rightarrow$  lower toughness

$\gamma = 12.3\%$

- No changes in microstructure or critical defects
- Poor creep resistance of cubic  $ZrO_2$
- Release of residual stresses  $\rightarrow$  lower toughness

$\gamma = 0.5\%$

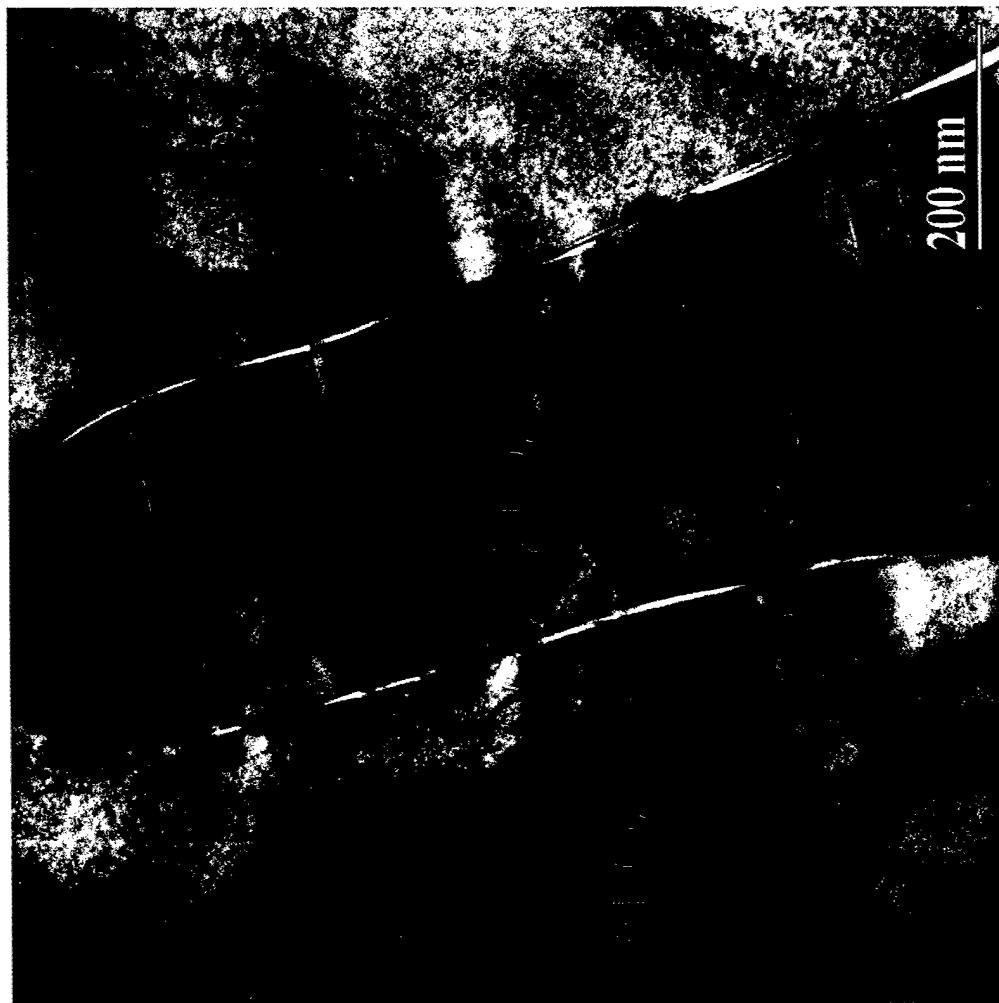
- Crack propagation at the  $ZrO_2$ - $Al_2O_3$  interface induced by:  
 $m \rightarrow t$  transformation between 700-900°C
- thermal residual stresses

## CONCLUSIONS

- $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$ ( $\text{Y}_2\text{O}_3$ ) eutectic oxides were processed using the laser-heated float zone method.
  - The microstructure of the composite (colonies vs interpenetrating) was controlled by changing the growth parameters.
  - The residual stresses and the crystalline structure of  $\text{ZrO}_2$  can be controlled by changing the  $\text{Y}_2\text{O}_3$  content.
- Mechanical properties of  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  eutectic oxides
  - Excellent strength ( $> 1.5$  GPa) at 300 K.
  - Excellent toughness ( $7.8$  MPa.m $^{1/2}$ ) at 300 K.
  - Fine microstructure stable up to 1800 K.
  - Very high strength retention at 1700 K ( $>800$  MPa). Presumably  $> 1$  GPa?

## *Microcracking*

Crack nucleation in  $\text{Al}_2\text{O}_3$  -  $\text{ZrO}_2(\text{m})$



Cracks nucleate at the  $\text{Al}_2\text{O}_3$ - $\text{ZrO}_2$  interface as a result of the  $\text{t} \rightarrow \text{m}$  transformation

## ***Microcracking***

Crack growth  $\text{Al}_2\text{O}_3$  -  $\text{ZrO}_2$ (m)

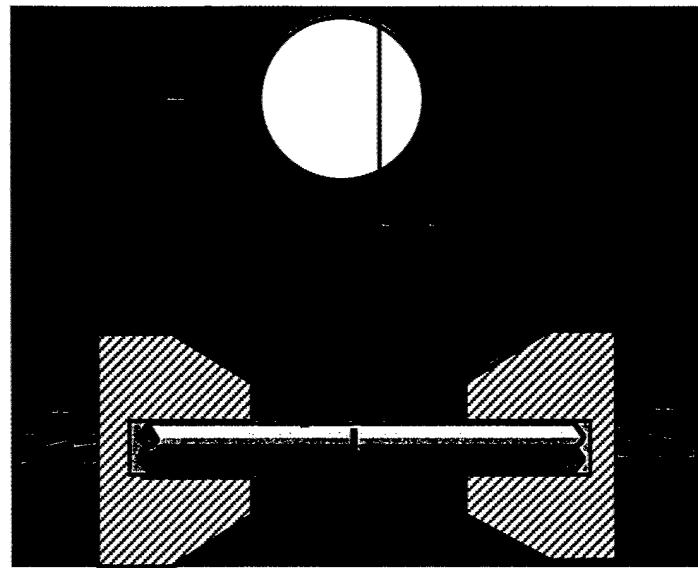
Cracks propagate upon cooling into the  $\text{Al}_2\text{O}_3$  phase, which is under tensile residual stresses.



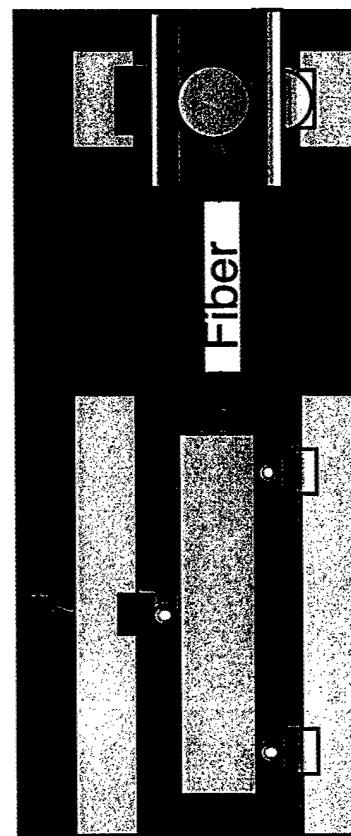
*Mechanical behavior*

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***Mechanical testing techniques***



**Fracture toughness**



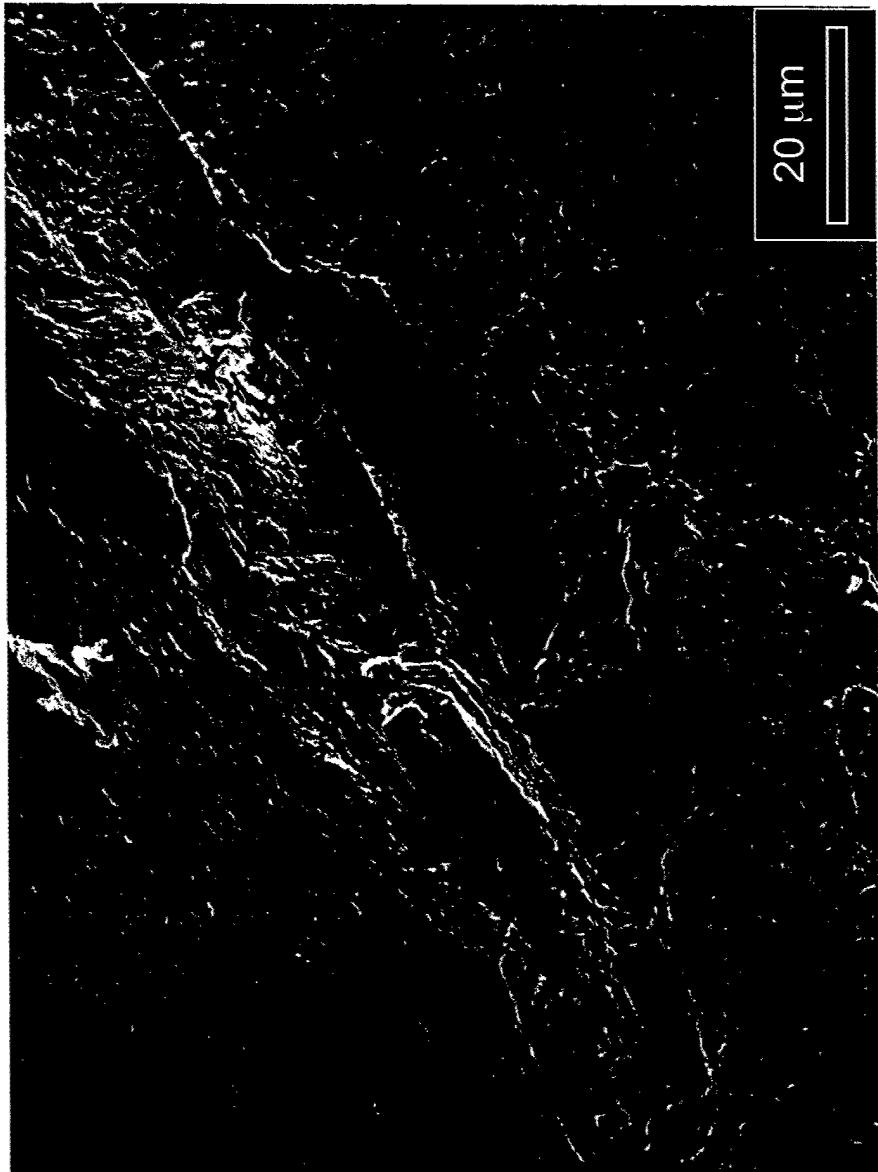
**Flexure strength**

### Ambient temperature

Colony structure ( $\Upsilon=10\%$ )

$$E \text{ (GPa)} \quad \sigma_t \text{ (MPa)} \quad K_c \text{ (MPa} \sqrt{\text{m}}\text{)}$$

$$343 \pm 7 \quad 1130 \pm 50 \quad 7.8 \pm 0.3$$



$$a_c = \frac{1}{\pi} \left[ \frac{K_c}{0.65 \sigma_f} \right]^2$$
$$a_c = 36 \mu\text{m}$$

## **Ambient temperature flexure strength**

Interpenetrating structure ( banding)

$\gamma$ (%)	0.5	3.3	12.2
$\sigma_f$ (GPa)	$0.6 \pm 0.1$	$1.15 \pm 0.08$	$1.13 \pm 0.05$
$ZrO_2$	mono	tetragonal	cubic

$\gamma=0.5\%$ :

- Low strength due to tensile residual stresses in  $Al_2O_3$  and microcracking

$\gamma=3.3$  and  $12.3$ :

- Excellent strength limited by inhomogeneities induced by banding

- No effect of  $t \rightarrow m$  transformation when  $\gamma=3.3\%$

### **Ambient temperature strength**

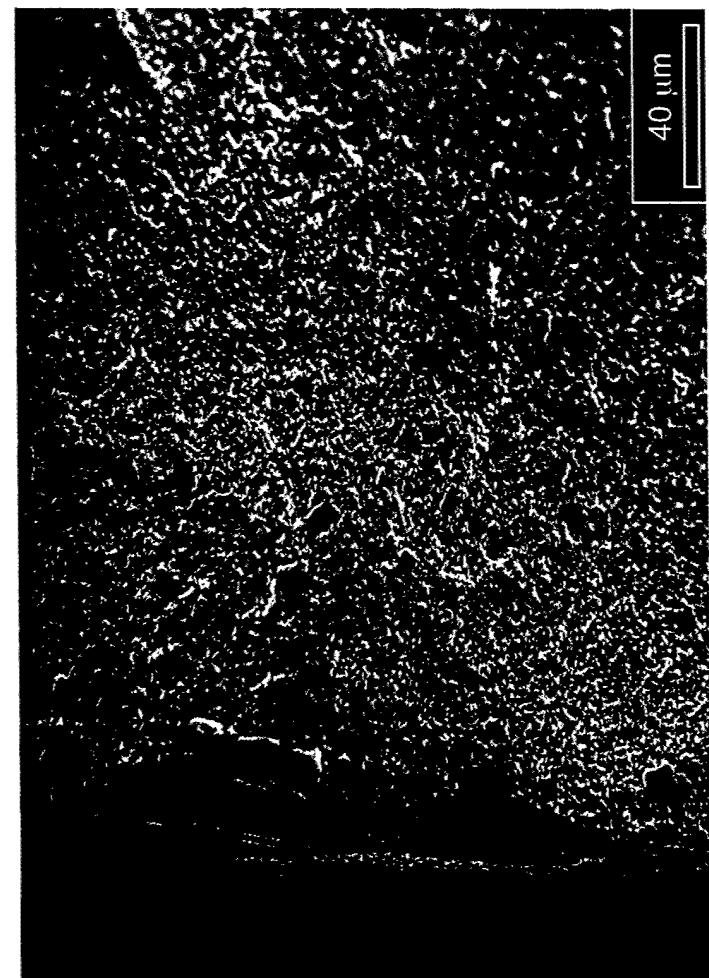
Interpenetrating structure (homogeneous)

1(%)3.312.2

$\sigma$

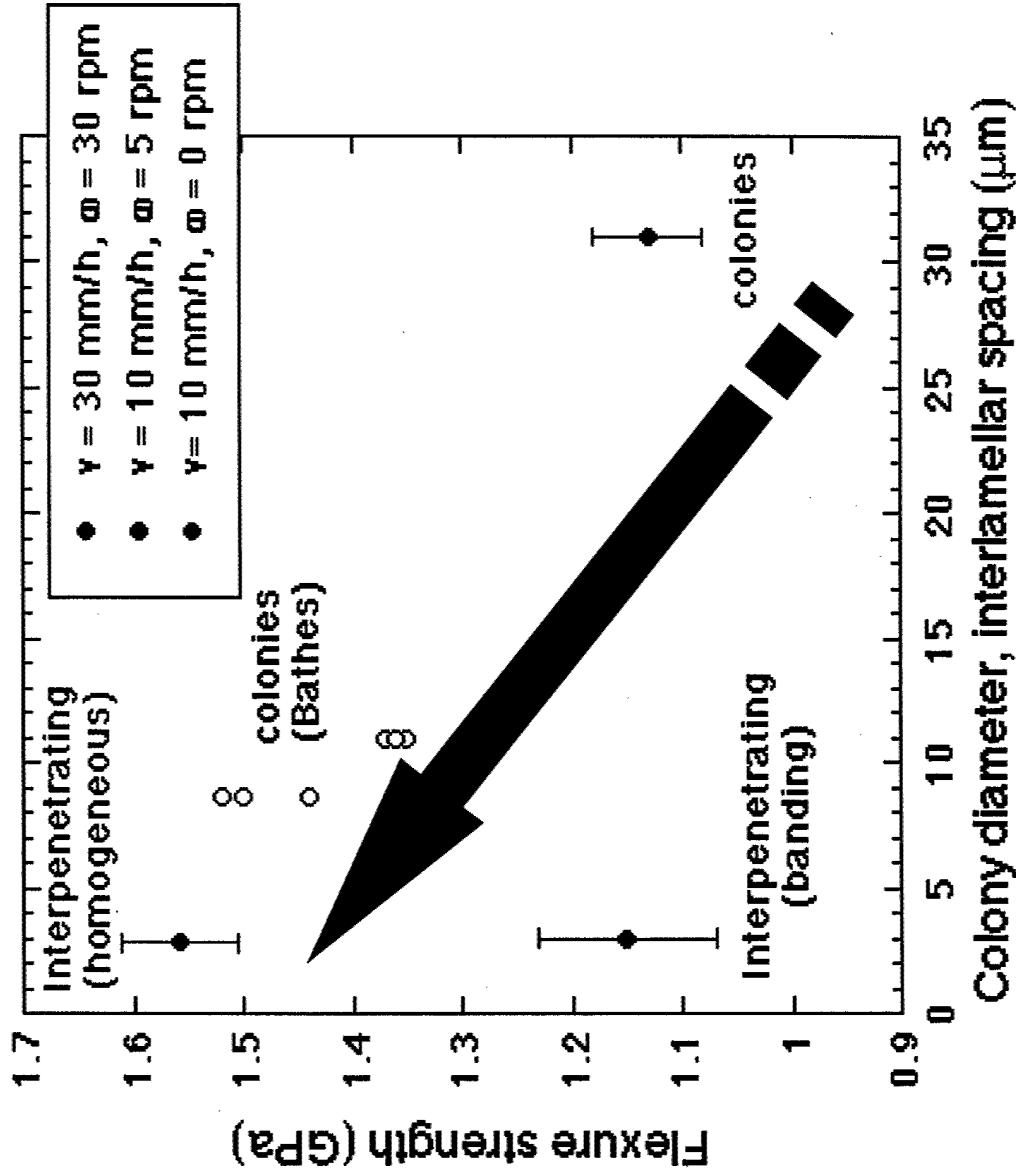
$\text{ZrO}_2$

$\sigma$



The critical defect of the homogeneous, interpenetrating structures are smaller

## Microstructure - flexure strength



## NANOSTRUCTURED MATERIALS BASED ON ALUMINA

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### ABSTRACT

Alumina and alumina-based compounds were prepared using high specific surface area  $\text{Al}_2\text{O}_3$  monoliths obtained by a novel preparation method. Impregnation with either liquid or vapor species followed by a thermal treatment under air or a reducing atmosphere leads to nanostructured spinels, mullite,  $\text{Al}_2\text{O}_3$ -metal or  $\text{Al}_2\text{O}_3$ -oxide composites.

### INTRODUCTION

Many technological applications require materials with a controlled microstructure or/and chemical composition. In addition, low density or/and high specific surface area are needed for catalysts, sensors, filtration membranes, composites. Alumina and alumina-based compounds like spinel  $\text{Al}_2\text{MgO}_4$  or mullite  $\text{Al}_6\text{Si}_2\text{O}_{13}$  are of special interest because of their thermal stability and mechanical properties. This paper describes the synthesis of these compounds and various  $\text{Al}_2\text{O}_3$ -metal or  $\text{Al}_2\text{O}_3$ -oxide composites with nanometric grain size starting from porous alumina precursors.

### NANOMETRIC ALUMINA AND $\text{SiO}_2$ -MODIFIED ALUMINA

The starting materials are monolith alumina preforms consisting of nanometric amorphous or  $\gamma$ -aluminas. In particular, we have used porous monolithic samples obtained by room temperature oxidation of Al plates through a liquid mercury layer [1]. The composition and the structure of hydrated alumina filaments produced by this way were described by Pinel and Bennett [2]. The new process that we have developed produces shaped alumina monoliths at a typical rate of about  $10 \text{ mm.h}^{-1}$  and the growth can be maintained during tens of hours. These alumina samples have a very light density ranging from  $0.01$  to  $0.05 \times 10^3 \text{ kg.m}^{-3}$  depending on the growth conditions.

After a dehydration treatment at 400°C,  $\text{Al}_2\text{O}_3$  amorphous monoliths are obtained with a nanostructure consisting of tangled filaments of about 5 nm diameter with large voids between them (fig. 1). The material crystallises first into  $\gamma$ -alumina at 870°C and then transforms into  $\theta$ -alumina above 1100°C. The average grain size is about 10 nm and the density remains very low ( $< 0.1 \times 10^3 \text{ kg.m}^{-3}$ ). At 1200°C-1250°C, transformation into  $\alpha$ -alumina occurs which leads to a microstructure with 200-300 nm grain size (fig. 2). Density increases by about one order of magnitude at the  $\theta \rightarrow \alpha$  transition and above 1350°C densification occurs by sintering of the  $\alpha$  alumina phase. Thus, various alumina samples with a controlled porosity can be prepared by adapting the thermal cycle.

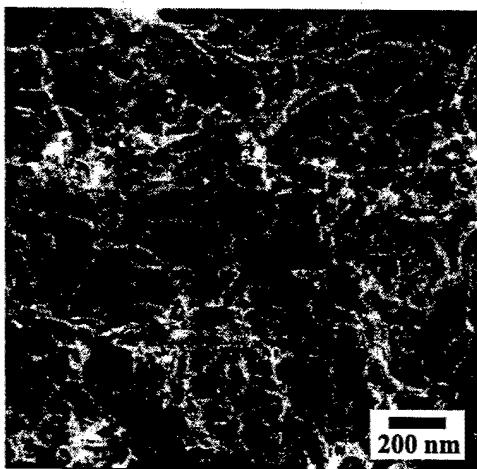


Figure 1 : raw alumina sample  
(second electron SEM image)

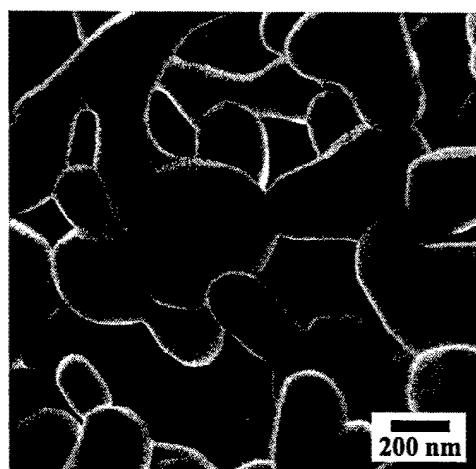


Figure 2 : after annealing at 1200°C  
(second electron SEM image)

The very high porosity of starting hydrated raw monoliths allows a rapid and homogeneous impregnation by gaseous species. In particular, a flow of silicon alkoxides diffusing inside the porous network is hydrolysed by the hydrated alumina surface. A remarkable modification of the thermal behaviour of alumina is obtained when a low amount of silica (about 6% weight  $\text{SiO}_2$ ) is incorporated by this way using trimethylmethoxysilane (TMES). Without Si addition, the specific surface area of the raw material ranges between 300 and  $420 \text{ m}^2 \cdot \text{g}^{-1}$  depending on preparative conditions. After crystallization, the specific surface area stays relatively high (around  $100 \text{ m}^2 \cdot \text{g}^{-1}$ ) and considerably decreases towards  $5 \text{ m}^2 \cdot \text{g}^{-1}$  at the  $\theta \rightarrow \alpha$  transformation. Silica addition delays the transformation into  $\alpha\text{-Al}_2\text{O}_3$  up to 1400°C instead of 1200°C without silica addition. This chemical modification stabilizes aluminas with high specific surface area at higher temperature as shown on Figure 3.

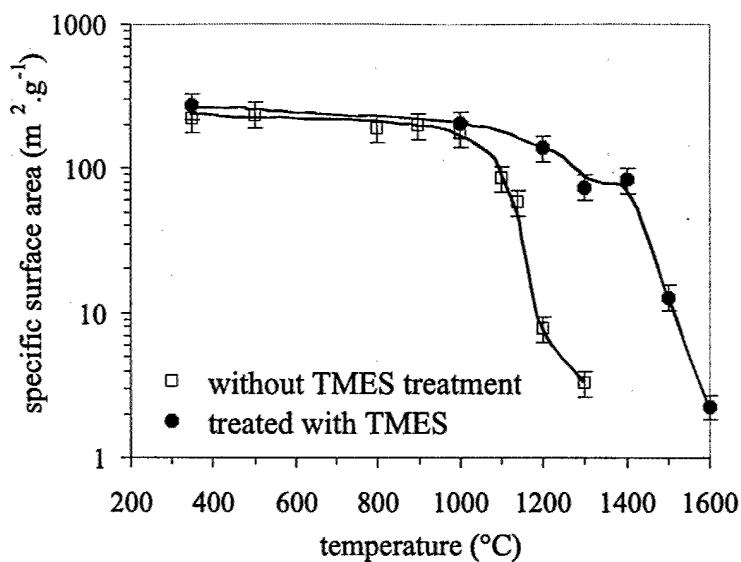


Figure 3 : Variation of the specific surface area versus temperature (4 hours annealing) for porous alumina impregnated or not by TMES.

## NANOSTRUCTURED ALUMINA COMPOUNDS

### a) nanometric mullite:

Similarly, silica can be incorporated using tetraethoxysilane (TEOS) vapour. This alkoxide with four hydrolysable functions permits higher silica additions than TMES. In particular, for the composition of mullite  $3\text{Al}_2\text{O}_3\text{-}2\text{SiO}_2$ , nanometric mullite monoliths are obtained after reaction. The average crystallite size determined from XRD line broadening is 10 nm at  $1000^\circ\text{C}$  and 30 nm at  $1200^\circ\text{C}$  (fig. 4). Transmission electron microscopy (TEM) images show that this size corresponds to crystalline particles (fig.5).

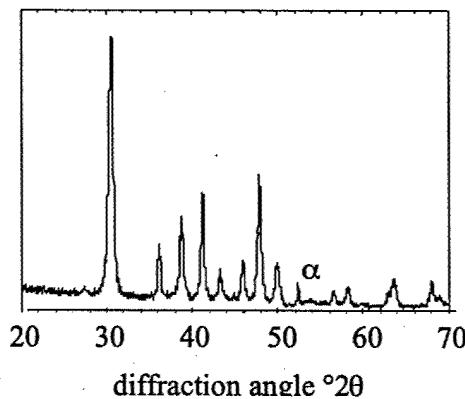


Figure 4 : X ray diffraction pattern of nanometric mullite prepared at  $1200^\circ\text{C}$

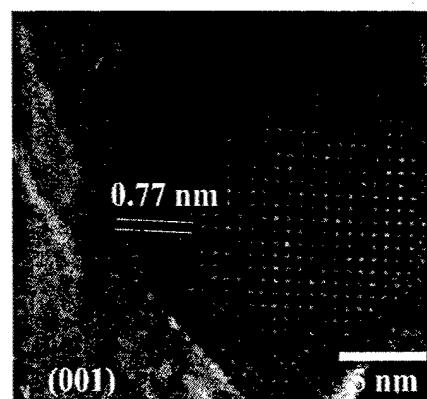


Figure 5 : HRTEM image of a mullite nanocrystal prepared at  $1200^\circ\text{C}$

b) nanometric spinels:

Liquid impregnation is another way for chemical species to be introduced. After absorption of aqueous solutions of divalent metal salts by porous alumina preforms, calcination in air at low temperature (200-500°C) leads to nanometric MO particles (M= Mg, Ni). A subsequent heating treatment produces the reaction with alumina to form  $MA1_2O_4$  spinel phases. For example, after impregnation of a porous alumina with a 300 nm grain size (fig. 2) with a magnesium nitrate solution, MgO is observed after annealing at 500°C, spinel appears at 900°C and the reaction is completed at 1200°C. After treatment at 1200°C, the spinel samples keeps the same microstructure as that of starting  $\alpha$ - $Al_2O_3$ . However, the transformation of each corundum grain into spinel produces aggregated spinel crystallites with a size around 100 nm. Similar behaviours and microstructures are obtained for  $NiAl_2O_4$  and  $CoAl_2O_4$  porous samples [3].

If the raw hydrated alumina is treated by TMES as previously exposed, spinels are formed at a lower temperature after a similar impregnation by Mg or Ni nitrate and annealing. Reaction into spinels occurs in that case at a finer scale. The reaction starts at 700°C and is completed at 1000°C in 4 hours for  $MgAl_2O_4$  and  $NiAl_2O_4$ . This process allows to obtain nanometric spinels (fig. 6) with a microstructure similar to that of figure 1. The crystallite size stays in the range of 10 nm up to 1000°C (fig. 7). These samples display a high specific surface area which is higher than  $40 m^2.g^{-1}$  for preparation at temperatures of 700°C to 1100°C.

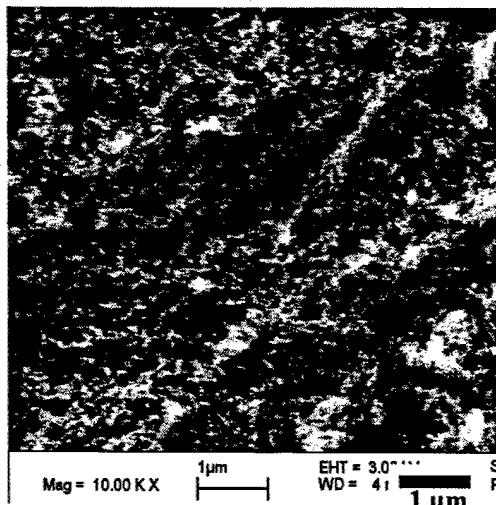


Figure 6 : SEM image of a nanometric  $NiAl_2O_4$  spinel prepared at 1000°C

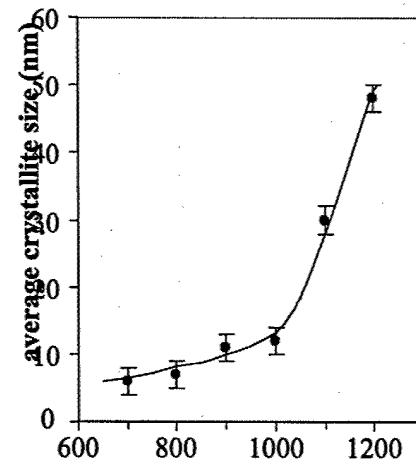


Figure 7 : Average crystallite size of  $MgAl_2O_4$  spinel after 4 hour annealing

## Al<sub>2</sub>O<sub>3</sub>-OXIDE and Al<sub>2</sub>O<sub>3</sub>-METAL NANOCOMPOSITES.

Particles of various oxides (TiO<sub>2</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>) were introduced on alumina preforms by liquid impregnation of salt solutions. The size of crystallites covering porous aluminas is in the range of 5 to 20 nm depending on conditions of calcination and crystallisation [3-4]. This technique has been also used to prepare WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub>/ Al<sub>2</sub>O<sub>3</sub> catalysts for cracking and skeleton isomerization of hexenes [5-6].

The reduction of nickel or cobalt oxides dispersed in  $\gamma$  or  $\alpha$  alumina under dihydrogen or a CO/CO<sub>2</sub> buffer atmosphere gives metal-ceramic composite samples. Another route used was to reduce the spinel formed by the reaction discussed previously. Depending on the preparative route, the temperature of reduction (between 650 and 1025°C) and the oxygen partial pressure (between 10<sup>-13</sup> to 10<sup>-20</sup> atm), metallic particles have a size distribution varying from 10 nm to 100 nm [7]. These composites consist of Ni or Co particles dispersed in a submicronic  $\alpha$  alumina porous matrix or in a nanometric  $\gamma$  or  $\theta$  phase (fig. 8).

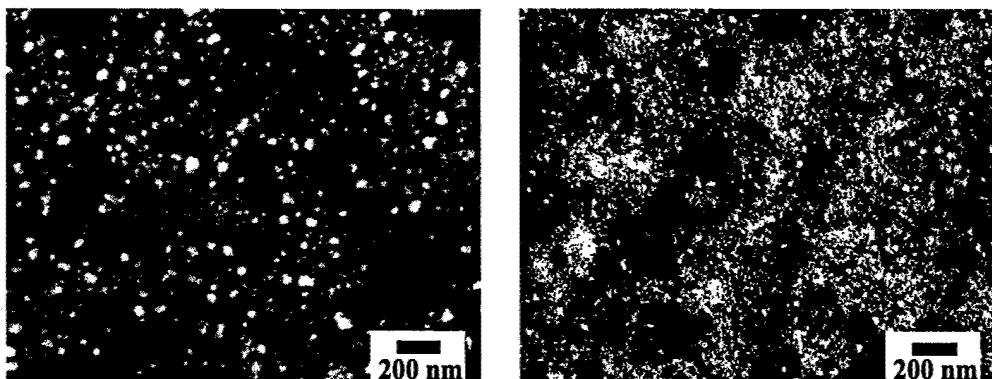


Figure 8 : Nanocomposites consisting of Ni particles dispersed in  $\gamma$  alumina obtained by reduction of NiO at 700°C under a CO/CO<sub>2</sub> controlled oxygen pressure ( $p_{O_2} = 10^{-20}$  atm). Left part : 10% volume Ni, right part: 5 volume% Ni. Backscattered electron SEM images.

## CONCLUSIONS

This paper presents various examples of preparation of nanostructured porous materials based on alumina. The insertion of chemical species by gaseous and liquid absorption into porous preforms followed by a thermal treatment leads to the synthesis of alumina compounds with a nanometric or submicronic microstructure. Metal-alumina nanocomposites can also be prepared by this way and recently carbon nanotubes were grown inside such aluminas from cracking of an organic precursor [8].

## ACKNOWLEDGMENTS

The work on metal-ceramic nanocomposites was achieved thanks to the support of the French-Chinese Association for Scientific and Technological Research (AFCRST) within the framework of the Advanced Research Programme on Materials PRA MX00-07.

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